SEMI-MICRO QUALITATIVE ANALYSIS

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PREFACE

Microchemistry, in its several branches, has advanced with remarkable strides during the past several decades. This is particularly true of the methods and technique of quantitative microanalysis and of chemical microscopy. In the field of qualitative analysis, aside from the great improvements in the methods of microscopic separation and identification, there has been developed a special technique, the drop-reaction method, semimicro in scale, in which the operations of qualitative analysis are conducted on a reduced scale and in which the microscope is not employed. This method occupies a position intermediate between the conventional macro technique and the highly refined micro methods.

About eight years ago, the authors, impressed by the advantages of the "drop" technique for instructional purposes in qualitative analysis, began a study of these new methods. Eventually a systematic scheme based on existing macro schemes was evolved, and the methods were tried with a small group of students in the summer session of 1931. Since then seven additional classes, mainly second-year students, in the winter and summer sessions, have received their instruction in elementary qualitative analysis through the medium of this new technique. Advanced and graduate students in our laboratories have also frequently availed themselves of these more rapid and sensitive methods.

It has been the aim of the authors to apply the methods and technique of microanalysis to the ordinary (macro) schemes of qualitative analysis with the objects: first, of confining the operations to drops or, at most, to one or two cubic centimeters of solution; second, of developing a micro scheme which could be placed in the hands of undergraduate students taking their first course in qualitative analysis; and third, by dispensing with the use of microscopes, of bringing the micro technique within practical pedagogic and economic reach of large laboratory classes of sophomore or even freshman students. Attention has been

focused on conducting separations, washings, filtrations and similar operations with usually not more than one cubic centimeter of solution and on performing final tests by means of drops. The procedures and methods worked out here can be employed by beginning students and require no previous special training.

The authors firmly believe that, in a beginning course in qualitative analysis, the fundamental theory, reactions and separations so characteristic of the older macro systems should not be sacrificed. These, after all, form the beginner's background and foundation in analytical chemistry. Accordingly, the conventional separations and identifying tests have been retained wherever possible, and these have been supplemented by the newer, more sensitive reactions. The methods here given may, if desired, be carried out with the usual reagents, only the scale of operation being reduced. With these objectives in view, utilizing the mass of available published information and adopting the technique originally described by others, the course of instruction presented in this book has been developed, a preliminary report of which has already been published.

Flexibility of the material has been sought so that the manual might serve the needs of the professional analyst, as well as the beginning student. The subject matter is arranged so that it can readily be adapted to long or short courses of instruction. The trained analyst will find among the new reactions described many shorter, more rapid and more delicate tests than are possible with the older methods.

The more important advances among the large mass of new material appearing in the recent chemical literature have been included. Only those tests which we have tried and found successful have been described in detail; others are merely mentioned and referred to. The references, which are given to the original papers as well as to *Chemical Abstracts*, will be found a convenient starting point for the advanced and more interested student who wishes to pursue the subject further.

The authors have been greatly encouraged by the hundreds of inquiries and requests for mimeographed material coming from teachers and others in this and foreign countries. They appreciate likewise the interest and cooperation of their many students who have aided in working out the details of the methods. Much

real help and inspiration has come from the publications of others, particularly from that standard authoritative text *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* by Fritz Feigl of Vienna.

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SEMI-MICRO QUALITATIVE ANALYSIS

INTRODUCTION

Analytical chemistry deals with the methods and principles involved in determining the composition of matter. A qualitative analysis tells **what** constituents are contained in a given material, and a quantitative analysis determines **how much**. Various chemical, physical and optical methods, devices and instruments are employed in this quest, and, where the qualitative analysis depends principally upon chemical properties, the methods consist, in general, of separating the constituents one from another by suitable chemical reactions and then of adding appropriate reagents which give distinctive identifying tests for the presence of the constituents sought. In a qualitative chemical analysis, in which the material under investigation must first be dissolved, the analysis for the detection of the cations (metals) proceeds separately from that of the anions (acid radicals). In practice, the methods resolve themselves into a series of separations by which individual ions or groups of ions are isolated, before identifying and confirmatory tests are applied.

During the long course of chemical history such schemes of separation and better and more sensitive tests have gradually evolved and the technique of conducting the manipulations has been greatly improved, so that, today, we have, as far as the scale of operations is concerned, three more or less distinct techniques. The first and oldest of these is the macro technique in which beakers, flasks, funnels and test tubes of the usual size are employed and where the volumes of solutions are relatively large, ranging from several cubic centimeters up to 100 cc. or more. On the other extreme is the truly micro technique, with its highly specialized, diminutive apparatus; the microscope is employed as an important adjunct and the volumes of test materials are usually not more than several cubic millimeters. Intermediate between these two is the special technique or mode of operation

upon which the procedures in this book are based and which has borrowed in the way of methods and appliances from the other two methods. It is partly macro and partly micro chemical.

Among the features which characterize and define this new technique are: first, the volumes of solutions and amounts of material are limited so that group precipitations, separations, washings and similar operations are generally confined to 1 cc. of solution; second, identifying tests are made with drop portions of test substance and reagents, the reacting solutions being brought together on spot plates, glass slides or drop-reaction paper; and, third, "filtrations" are conducted, ordinarily, with a small hand centrifuge. The microscope is not employed in the methods described here.

Microchemistry embraces all methods of handling, investigation and analysis in which relatively small amounts of materials are involved. The methods of microchemical analysis include, in a broad way, such operations as blowpipe analysis, chemical microscopy, spectroscopy and colorimetry as well as the usual operations of qualitative and quantitative analysis conducted on a small scale. The microscope has long been used in analytical work, reliable methods having been developed by Behrens, Kley, Schoorl, Chamot, Emich, Benedetti-Pichler and others. Emich, who may be regarded as the founder of modern microchemistry, has described many of these methods in his two classical publications. Quantitative microanalysis has been brought to its high state of perfection largely through the labors of Fritz Pregl.

In the field of qualitative analysis, during the past fifteen years or so, a tremendous amount of work has been done, the object of which has been to find extremely sensitive reagents and specific reactions which would give tests for ions in the presence of other ions. The current chemical literature contains a wealth of published work of the results of such investigations. Much of this work is microchemical in nature in that the operations are conducted on a small scale with relatively small amounts of test substances and small volumes of solution. Noteworthy contributions have been made in qualitative microanalysis by Gutzeit, Tananaev, Van Nieuwenberg, Feigl and his co-workers and others. To Feigl in particular much credit is due for his contribution, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen,* which today is the authoritative reference. Feigl gives an excellent discussion

of a considerable number of specific and highly sensitive reactions, conducted as spot and drop tests, less attention being given to systematic separations. Gutzeit has published a simplified scheme of separation and has recommended many organic and inorganic reagents. Similarly, Heller and Krumholz, and separately both Krumholz and Heller, have worked out schemes and special microchemical tests. Recently Van Nieuwenberg has published a scheme of analysis which follows, in its essentials, the conventional macro scheme.

There are no sharp boundaries between the three techniques previously defined, and, obviously, there is a certain overlapping, yet the technique is necessarily determined by the amount of material handled, and this in turn depends upon the size of the sample, the weight of each constituent in the sample and the volume of the solution. The whole matter is governed, in practice, by the conditions which it is possible to set up in order to obtain a fairly sensitive positive test for the presence of any given constituent. By the term "sensitivity" is meant the quantity of material which responds to the test reagent; if the quantity of test ion refers to its concentration, i.e., the amount present in a given volume, the limit of sensitivity is reached when a more dilute solution fails to give the test. If the absolute quantity of test substance, usually expressed in weight, is referred to, the sensitivity of a reaction is expressed in terms of actual weight of the test ion. The unit of microchemical weight is 1 microgram (1 μg.), or 1 gamma (1 γ), i.e., 0.001 milligram, or 0.000001 gram. Accordingly, on this definition of sensitivity, the limit of identification ranges from 1 mg. to much less than 0.1 μg., depending upon the technique employed. The sensitivity of a test depends, too, on the amounts of other substances present in the mixture when the test reagent is applied, for which the term "limiting proportions" is used.

Since, to date, very few absolutely specific tests have been discovered, methods of separation and isolation must be introduced, in order to free the ion, whose identification is being sought, from other constituents which interfere with the final test. In such schemes of separation losses are inevitable so that, as a general rule, a much greater quantity of each constituent must be taken as sample than corresponds to the minimum amount called for by the sensitivity. Years of experience with the systematic schemes

of analysis presented in this book have shown that with 1 mg. of each cation constituent in the sample, in 1 cc. of solution, ample amounts survive the separations so that *distinct* tests are obtained, with the exceptions of bismuth and the alkaline earth metals where about 3 mg. are required. The amounts of the anions vary, but a safe limit is about 5 mg.[1]

The schemes of analysis described in this book are not claimed to be perfect, and undoubtedly, as time goes on, the methods will be greatly improved. For the beginning student, the accuracy is about the same as with the macro scheme. Until he acquires the necessary skill, care and dexterity, the time consumed for an analysis is about the same as in the older technique. He must work with greater care and especially guard against losses, for sometimes the spilling of even a few drops may ruin the entire analysis. After the analyst has gained some experience with this technique, the analyses become very rapid.

The operations and apparatus of ordinary qualitative analysis have their counterpart in this new technique. Except for a small hand centrifuge and certain other simple apparatus, the appliances are in general miniatures of those used in ordinary analysis. They are easily procured and cost little compared to the usual macro equipment. A satisfactory hand centrifuge can be obtained for about eight dollars. The centrifuge tubes may be purchased or else made from Pyrex glass by the local glassblower. The test tubes are the 2-cc. biological tubes. Special drop-reaction paper, such as Schleicher and Schüll's paper No. 601, can readily be obtained. Glass slides, spot plates, reagent vials, medicine droppers, etc., complete the simple and inexpensive equipment. In a following section (see page 6) are given some suggestions and hints to the instructor regarding laboratory administration together with some instructions to the student.

The technique employed in carrying out the methods described in this manual is simple and so easily acquired that no special provision in the form of preliminary experimentation is made. The more important operations and manipulations are described below.

Precipitation.—Precipitations are carried out in centrifuge tubes, in test tubes, on spot plates, glass slides and drop-reaction

[1] Investigation is now in progress to determine the sensitivities of the tests, and the minimum amounts of sample needed, under the working conditions of the schemes here presented.

paper. In the first method, a drop of the precipitating agent is added to a drop of solution in a centrifuge tube. The advantage of this procedure lies in the ease with which the precipitate may be observed after centrifuging, and the facility with which a separation can be carried out.

In the spot-plate method, a drop of the solution to be tested is brought into contact with a drop of the precipitating agent in the cavity of a spot plate. This method is very effective for detecting the formation of colored precipitates. Black spot plates are used for observing white precipitates.

If the precipitation is to be conducted on a glass slide, a drop of the solution and one of the precipitant are placed side by side on the slide and the two are mixed by means of a platinum wire. When heating is necessary, the drops are placed as near to one corner of the slide as possible and the heat from a micro burner cautiously applied.

Color Reactions.—Many of the color reactions with organic reagents by which certain ions are detected are carried out on dense blotting paper known as drop-reaction paper. Such methods are usually more sensitive than conducting the same reaction on a spot plate or glass slide, owing to the concentration of the solutions in the capillary pores of the paper.

With certain of these reactions, the colors are brought out or "developed" by allowing hydrochloric acid vapor or ammonia fumes to come into contact with the reaction mixture on the paper. This is done by holding the reaction paper in the fumes evolved either by heating a few drops of concentrated HCl or NH_4OH, as the case requires, in the micro crucible or else by merely passing the paper over the mouth of the reagent bottle containing the concentrated acid or ammonia.

Filtration.—The operations of filtration and washing are conducted either in a centrifuge tube or on a glass slide, depending upon the method by which the precipitate was produced. In the former case, after centrifuging, the supernatant liquid is withdrawn by means of the capillary pipet. If washing of the precipitate is required, a few drops of wash water are added, the precipitate stirred with a platinum wire, the mixture again centrifuged and the supernatant liquid drawn off. When filtering and washing on a glass slide, the liquid surrounding the precipitate is withdrawn by placing a small wad of cotton near the edge of the solution and pushing this into the drop with the cotton

in the opening of a micro capillary pipet and applying suction by releasing the pressure on the compressed rubber bulb.

Occasionally, when close examination of precipitates is desired, filtration by means of the suction flask is resorted to. A piece of filter paper of proper diameter is punched out with a cork borer and placed in the funnel. The solution to be filtered is then placed in the funnel and suction applied by the mouth through a rubber tube attached to the flask.

Evaporation.—Evaporations are best conducted by transferring the solution to a crucible and heating with a micro burner. Considerable care is necessary in this operation to prevent losses due to spattering. Occasionally liquids are evaporated from glass slides or watch glasses.

Evolution of Gases.—A drop of solution to be tested is placed in a test tube, a drop of reagent added and a small funnel in a cork is inserted. Filter paper moistened with the test reagent is placed in the mouth of the funnel and the tube gently warmed, causing the evolved gas to come in contact with the paper.

NOTES ON LABORATORY WORK

Suggestions to the Instructor.—An ordinary laboratory with its standard furniture and appointments may be pressed into service as a microchemical laboratory, though the ideal arrangement is a special room furnished with low desks and low stools similar to those used in laboratories of chemical microscopy. Since there is little occasion for the student to leave his desk, stools might well be provided for his comfort, where he can remain seated, with his block of reagents and a centrifuge within reach. Laboratory supply houses now carry a complete line of equipment such as centrifuges and tubes, white and black spot plates, drop-reaction paper, micro crucibles and burners, glass slides, etc. For the student's individual set of common reagents and the common acids and bases, 30-cc. bottles provided with medicine droppers have been found satisfactory. Small vials with screw caps and droppers are convenient for other liquid reagents. A block of 2-inch plank, 6 in. by 6 in., bored with ¼-inch holes, serves well for holding the set of tubes containing the solid reagents as well as for the centrifuge tubes and test tubes.

In the appendix is given a list of apparatus intended for each

student. Part of this constitutes the permanent equipment of each locker, the remainder being secured by the student from the supply room. This equipment has been found ample for the needs of the work of the course.

A list of solid and liquid reagents will also be found in the appendix. Stock bottles, holding 100 cc. of each liquid reagent, may be kept on a reagent shelf, from which the student may fill and replenish his individual supply. Only a few cubic centimeters of each will generally suffice for the semester's work. Stock test solutions of the cations (10 mg. per cc.—see appendix) are convenient, from which the student can supply his own needs by diluting 1 cc. with 9 cc. of distilled water.

Hydrogen sulfide may be generated in individual generators, or by heating a mixture of sulfur and paraffin in asbestos, in a test tube provided with a delivery tube. This handy mixture may be purchased under the trade name of "Aitchtuess" or prepared in the supply room. A small wash bottle and a small suction flask will be found useful, although neither is indispensable.

Instructions to Students.—Carefully check over the contents of the locker assigned you and report missing or damaged apparatus. Procure the non-returnable apparatus if this has not been supplied. Seal the piece of platinum wire in a short length of glass tubing. Draw out a medicine dropper to a thin capillary point by heating in a hot flame; this will be your capillary pipet. Supply yourself with the liquid and solid reagents as directed by the instructor. With these chores done you are ready for the interesting and fascinating work which lies ahead of you.

PART I

FUNDAMENTAL PRINCIPLES OF QUALITATIVE ANALYSIS

The methods employed in qualitative analysis consist, in general, of separating the constituents from one another by suitable chemical reactions and then of applying appropriate reagents which give distinctive identifying tests for the presence or absence of the constituents sought. The correct selection of reactions for carrying out the necessary separations and identifying tests must rest upon the properties and characteristics of the element concerned; hence, from the experimental side, we must have a thorough knowledge of the behavior of the common metals and acid radicals whose analysis is considered in this elementary book. From the theoretical side, to understand how a reaction proceeds and to interpret the results properly, we must consider the laws governing reactions; and, since most of the chemical changes take place in solution, the laws and behavior of solutions become of fundamental importance. Little real intelligent progress can be made unless the theory is understood, properly appreciated and correctly applied.

SOLUTIONS, REAGENTS AND REACTIONS

Solutions

When a small amount of sugar or sodium chloride is added to water the solid disappears in the liquid, forming a homogeneous mixture which we call a solution. All solids show a tendency to dissolve in liquids, the amount of different solids taken up by a given amount of liquid varying between wide limits. Liquids may also dissolve in solids or in other liquids. Gases, too, show this property of dissolving in liquids and in solids. Thus it is possible to have solutions consisting of solids, liquids and gases

dissolved in liquids, as well as solids, liquids, and gases dissolved in solids.

The solid in a solid-liquid system is referred to as the **solute**; the liquid is the **solvent**. Where one liquid is dissolved in another, that liquid which is present in greater amount is the solvent and the other liquid is the solute. Water is the commonest solvent used in the chemical laboratory, and throughout qualitative analysis we deal very largely with aqueous solutions. Solid inorganic substances are the main solutes, although certain organic materials as well as some liquids and gases constitute the solutes in some instances. The preparation of solutions will be more fully discussed in a later section.

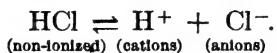
A true solution is one in which the solute is disintegrated down to at least molecular dimensions and uniformly distributed throughout the solvent. We may, however, have uniform distribution of a substance in a liquid in which the dispersed substance consists of aggregates of molecules; colloidal solutions and suspensions are of this type. Throughout this book, the word solution will be used to designate true solutions, and in fact, aqueous solutions will be implied thereby.

Properties of Aqueous Solutions.—Since the solutions with which we so largely deal in qualitative analysis consist of solids, liquids and gases dissolved in water, we must inquire into the behavior of dissolved matter and the effect of the solute on the properties of the solvent. Experiment shows that many of the properties of water are altered remarkably when dissolved material is present. Thus pure water freezes at 0° C., boils at 100° C. under 1 atm. pressure and exerts a vapor pressure of a definite magnitude at any specified temperature. But when, for example, sugar or sodium chloride is added to water, the freezing point of the water is lowered, the boiling point is raised and the vapor pressure is lowered, the extent of the change in these properties varying with the amount and nature of the solute present. The osmotic pressure of the solution, too, increases with increased concentration.

The properties of solutions have been extensively investigated, and as a result of much study and experimentation the conclusion was reached, many years ago, that solutes belong to either one of two classes with respect to their behavior when in aqueous solution. Compounds like sugar, glycerine, urea, and organic com-

pounds in general when present in equimolecular proportions, produce the same lowering of the freezing point and the same elevation of the boiling point of pure water. In fact, one gram-molecular weight of any of the compounds of this class, dissolved in 1000 g. of water, will lower the freezing point 1.86° C. and raise the boiling point 0.52° C. Solutions of this kind do not conduct the electric current. Inorganic compounds, however, as a general rule, cause a greater change in the above properties than would be anticipated for solutions containing the same number of molecules. The behavior of this class of solutes is abnormal when compared to that of organic compounds of the same concentration. Solutions of inorganic acids, bases and salts readily conduct the electric current. When physical properties of the kind here discussed are used as the basis for molecular-weight determinations it is found that compounds of the class to which sugar belongs give correct values while the inorganic compounds yield values that are too low.

The Phenomenon of Ionization.—To explain the abnormal behavior of dissolved acids, bases and salts, Arrhenius, in 1885, proposed the theory of ionization. This assumes that when acids, bases and salts are dissolved in certain liquids, particularly water, the molecules of the solute dissociate or ionize to a greater or less extent into positively and negatively charged particles called ions, those bearing positive charges being called cations and those with negative charges anions. Compounds showing this behavior are called electrolytes. The extent of the dissociation depends upon the nature of the solute, the concentration, the temperature and the solvent. The ions behave as independent units irrespective of the nature of the compound from which they are derived, and when two solutions of electrolytes react they show the behavior only of the constituent ions. The phenomenon of ionization can be indicated as a reversible chemical reaction between the dissolved non-ionized molecules and the cations and anions resulting therefrom. Thus for hydrochloric acid the ionization can be indicated by the reaction:

$$\underset{\text{(non-ionized)}}{HCl} \rightleftharpoons \underset{\text{(cations)}}{H^+} + \underset{\text{(anions)}}{Cl^-}.$$

Solubility.—The extent to which a solute will be taken up by a given amount of solvent under definitely specified conditions is a characteristic property, its solubility. The amounts of dif-

ferent substances which will dissolve in a definite quantity of water, say 1 liter, vary considerably. A solution is said to be saturated when the dissolved material is in equilibrium with an excess of undissolved solute. Inasmuch as these differences in solubility constitute a most useful means in qualitative analysis of separating one substance from another, we must study solubility relationships and select reactions which will differentiate substances on the basis of their solubilities.

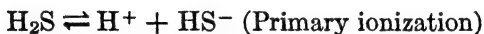
If more than the saturation amount of solid is added to a solvent, the excess will remain as undissolved solid, except in those cases where supersaturated solutions form, a condition which is unstable. An idea of the wide variation in the amounts of different solid solutes required for saturated solutions can be gained by reference to the table of quantitative solubilities in the appendix. This table shows the amounts of different inorganic salts needed to saturate 100 cc. of water. The solubility of a solid in water increases, as a general rule, with increase in temperature, and only slightly with increase in pressure. An important application of the general equilibrium theory involving saturated solutions of difficultly soluble salts is discussed in a later section.

Two liquids may be totally or only partially soluble in each other. Thus water and alcohol mix in all proportions, and no limit can be placed on the saturation amount. Carbon disulfide is only slightly soluble in water, and if the solubility is exceeded, the excess will remain as a second liquid layer; we speak of these two liquids as being practically immiscible in each other. Chloroform, ether, benzene and many other organic liquids form similar two-liquid layer systems with water.

The amount of a gas which will dissolve in a definite volume of water under existing temperature and pressure conditions, too, is fixed by its saturation quantity, and any excess escapes as free gas. In general, the solubility is decreased with rise in temperature and increased with an increase in the pressure. Some gases, such as hydrogen chloride and hydrogen sulfide, merely dissolve in water, whereas others, such as sulfur trioxide and ammonia, react with water. The solutions of gases in water, whether or not reaction takes place with the solvent, comprise some of our most important and commonest reagents. A more detailed discussion of gaseous-liquid systems is given in a later section.

In an aqueous solution of HCl, there exist a certain amount of hydrogen ions, an equal amount of chloride ions, side by side with a certain amount of non-ionized molecules of hydrochloric acid, the proportion depending upon the temperature and the total amount of solute present. Acids having two replaceable hydrogen atoms ionize in two stages, designated as the primary and the secondary ionization stages, respectively. Sulfuric acid and hydrogen sulfide are two such dibasic acids. In a H_2S solution the two stages of ionization are presented thus:

$$H_2S \rightleftharpoons H^+ + HS^- \text{ (Primary ionization)}$$

$$HS^- \rightleftharpoons H^+ + S^= \text{ (Secondary ionization).}$$

Tribasic acids ionize in three stages, designated as the primary, secondary and tertiary ionization stages (see, for example, Table I, page 14, the ionization of H_3PO_4). The primary ionization always takes place to a much greater extent then the secondary, and the secondary more than the tertiary. Acids are defined on the basis of the ionization theory as substances which are capable of yielding hydrogen ions.

The ionization of bases shows the same general behavior, the dissolved molecules ionizing more or less into metallic ions and hydroxyl (OH^-) ions. Salts ionize into positively charged atoms or radicals (cations) and negatively charged atoms or radicals (anions).

If the extent to which different acids, bases and salts ionize is compared for solutions containing equal gram-molecular weights of the solute, and at the same temperature, it will be found that this varies considerably with different electrolytes. Electrolytes in moderately dilute solutions, in which the proportion of the ionized to the non-ionized part is large, are strong electrolytes. Examples of strong electrolytes are solutions of HCl, NaOH, NaCl and, as a general rule, most inorganic salts. On the other hand, weak electrolytes are those in which the tendency to ionize in moderately dilute solutions is relatively small, such as solutions of NH_4OH, $HC_2H_3O_2$, H_2S, H_2CO_3 and water itself.

Table I shows the percentage of ionization of solutions of common acids, bases and salts each contining 0.1 of the molecular weight of the solute in grams, in a liter of solution. Solutions containing this amount of solute are known as 0.1 molar solutions.

TABLE I

PERCENTAGE IONIZATION OF COMMON ACIDS, BASES AND SALTS IN 0.1 MOLAR SOLUTIONS AT 18° C.

Acid	Ionization Reaction	Per Cent Ionized
Hydrochloric	$HCl \rightleftharpoons H^+ + Cl^-$	92.0
Nitric	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	92.0
Nitrous	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	8.0
Formic	$HCHO_2 \rightleftharpoons H^+ + CHO_2^-$	4.5
Acetic	$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$	1.34
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	0.01
Sulfuric	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	90.0
	$HSO_4^- \rightleftharpoons H^+ + SO_4^{=}$	60.0
Oxalic	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$	40.0
	$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{=}$	1.0
Carbonic	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	0.12
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}$	0.0017
Hydrosulfuric	$H_2S \rightleftharpoons H^+ + HS^-$	0.05
	$HS^- \rightleftharpoons H^+ + S^{=}$	0.0001
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	27.0
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{=}$	0.1
	$HPO_4^{=} \rightleftharpoons H^+ + PO_4^{\equiv}$	0.0001
Water	$HOH \rightleftharpoons H^+ + OH^-$	0.0000002
Base		
Sodium hydroxide	$NaOH \rightleftharpoons Na^+ + OH^-$	90.5
Ammonium hydroxide	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.31
Calcium hydroxide	$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$	75.0
Salt	**Examples**	
Uni-univalent	KCl, $NaNO_3$ NH_4Cl, $NaC_2H_3O_2$	80.-85
Uni-bivalent	$CaCl_2$, K_2SO_4, etc.	70.-75
Bi-bivalent	$MgSO_4$, $CuSO_4$, etc.	35.-45

Note that for acids the degree or percentage of ionization varies from 92.0 per cent for HCl to 0.01 per cent for HCN, for solutions of equal strength, and that the primary ionization for polybasic acids takes place to a much greater extent than the secondary and

tertiary. Note, too, that NaOH is typical of a strong base whereas NH_4OH is a weak base. The behavior of salts depends upon the type, and as a general rule for such concentrations as are usually employed in laboratory reagents the percentage of ionization is large. A few salts, notably certain salts of mercury, lead acetate, ferric acetate and a few others, are exceptions in that their ionization is abnormally weak.

Ionization and Concentration.—The foregoing discussion and Table I have shown that the percentage of ionization differs widely for different electrolytes in solutions of the same concentration. For the same electrolyte the ionization varies with the concentration, if temperature and other factors remain unaltered. That is, the more dilute the solution, the greater will be the degree of ionization. If we take, for example, a liter of a 0.1 molar solution of acetic acid, in which the degree of ionization is 1.34 per cent, and dilute it with 9 liters of water, the resulting solution will be only one-tenth as concentrated; and if we measure, by electrical conductivity or other methods, the new degree of

TABLE II

VARIATION OF PER CENT IONIZATION WITH CONCENTRATION AT 18° C.

Electrolyte	Concentration of Electrolyte in Mols per Liter			
	1 *M*	0.1 *M*	0.01 *M*	0.001 *M*
HCl	80.0	92.0	97.2	99.0
HNO_3	85.0	92.0	96.9	99.0
$HCHO_2$ at 25° C	1.5	4.5	13.4	35.8
$HC_2H_3O_2$	0.4	1.34	4.17	11.7
NaOH	77.0	90.5	93.3	97.1
NH_4OH	0.4	1.31	4.07	11.7
NaCl	74.1	85.2	93.6	97.7
$AgNO_3$	....	81.4	93.1	97.7
$NaCHO_2$	59.5	85.4	93.1	....
$NaC_2H_3O_2$	52.6	77.9	89.4	....
NH_4Cl	74.7	85.3	94.0	....
K_2SO_4	....	67.3	83.2	93.7
$MgCl_2$	....	72.8	85.1	93.9
$MgSO_4$	....	40.3	59.6	82.3

ionization, we will find it to be 4.17 per cent at 18° C. Further dilution will result in still greater ionization, until in extremely dilute solutions there is no further increase in ionization. When this point of infinite dilution is reached the solution is 100 per cent ionized.

The variation of the degree of ionization with concentration is shown in the preceding table for two strong acids, two weak acids, a strong base, NaOH, a weak base, NH_4OH, and a number of salts.

Note that, for the strong acids, strong bases and salts, the ionization is nearly complete in 0.001 molar solution, and that for the weak acids and base much greater dilution than shown here will be required to bring about complete ionization. The distinction between a strong and a weak electrolyte involves the concentration, and, as noted in a previous paragraph, a solute is considered a strong electrolyte if the proportion of ions to the non-ionized fraction is large when the total amount of dissolved solute is relatively large. Acetic acid and ammonium hydroxide are not considered strong electrolytes because it is only in extremely dilute solutions that the concentration of ions predominates over the non-ionized molecules.

The increase in ionization with increase of dilution will be discussed in a later section when the equilibrium relationships in solutions are treated in a quantitative way.

Ionization and Temperature.—With an increase in temperature most electrolytes show a decrease in the percentage of ionization. Thus in 0.08 molar solutions of HCl at 18° C. the percentage ionized is 92.3; at 100° C. it is 89.7. For the same conditions in the case of $HC_2H_3O_2$ the values are 1.5 and 1.17 per cent, respectively. Water is an exception to this rule, the ionization increasing somewhat with rise in temperature.

Effect of Solvent on Ionization.—Electrolytes ionize to a greater extent in water than in any other solvent. Water is also the commonest solvent. Other ionizing solvents are liquid ammonia, liquid hydrogen cyanide and liquid sulfur dioxide. The ability of a solvent to bring about ionization is related to its dielectric constant, and, in general, the greater the dielectric constant, the better the medium for ionization of the solute to take place. The presence of other dissolved substances also influences the extent of ionization of many solutes.

Reagents

The Solutions Employed in Qualitative Analysis.—In the laboratory work of qualitative analysis, the student is concerned with the test substances of known and unknown composition as well as with the many reagents that are employed. The preparation of solutions of samples to be analyzed as well as of certain of the reagents to be used is an important part of the laboratory work. Regarding the test substances it may be said that it is best first to study the analytical properties and reactions of the elements separately and to follow this experimental study by the analysis of mixtures of known composition before the analysis of samples of unknown composition is undertaken. For the purpose of this preliminary experimentation, so called test solutions, to be described in a later paragraph, are usually provided. Solutions of samples must also be made by dissolving the samples in water, acids or other solvents according to the methods described in Part IV of this book.

The reagents are, generally, aqueous solutions and are prepared by:

(*a*) Dissolving solids in water.
(*b*) Dissolving gases in water.
(*c*) Dissolving liquids in water.
(*d*) Diluting " concentrated " reagents.

Methods of Expressing the Concentration of Solutions.—The strength of a solution may be expressed in a number of ways; the following types of solutions, with respect to the method, units or system used to designate the concentration, are recognized in analytical chemistry.

1. *Test Solutions.*—The so-called test solutions contain the individual ions whose characteristic reactions and properties are studied in the " Preliminary Experiments." A series of cation test solutions, made whenever possible from the nitrates of the metals, are usually prepared and placed at the disposal of the student. In these solutions the cation content is kept uniform, each cubic centimeter of solution containing 10 mg. (0.01 gram) of the cation. These solutions therefore represent one type of concentration measurement. A list of cation " stock " test solutions is given in the appendix. The preparation of the test solutions involves a simple direct proportion calculation which may

be illustrated by the silver test solution. Since each cubic centimeter is to contain 10 mg. or 0.01 gram of the cation, 1 liter (1000 cc.) will contain 1000 × 0.01 or 10 grams of silver. If silver nitrate is used to furnish this Ag^+ ion, assuming complete ionization of the $AgNO_3$, it is then a simple matter to calculate the weight of $AgNO_3$ required to furnish 10 grams of silver from the following proportion:

$$\underset{(107.88)}{Ag} : \underset{(169.89)}{AgNO_3} = 10 : x$$

from which x, the weight of $AgNO_3$ required, is found to be 15.75 grams.

The advantage resulting from the use of test solutions of uniform, known strength lies in the fact that the sensitiveness of the test can be studied with better results. Some judgment can be formed of the relative amounts of each component present in a mixture if the preliminary work is carried out with solutions of known and equal strength. In this way a qualitative analysis becomes an approximate quantitative one. The student should always exercise judgment in distinguishing traces from considerable quantities of a constituent found in the course of an analysis.

2. *Empirical Solutions.*—The solutions resulting from dissolving solid samples and a great many of the reagent solutions represent another type in that there is nothing uniform in regard to their concentrations, each individual solution being made up of a strength best suited for its particular use. These may be called empirical solutions. In this connection examine the list of reagents in the appendix. The concentration of these solutions may be expressed in grams of solute per liter or per cubic centimeter. If expressed in grams of solute or its equivalent per cubic centimeter, the term titre is sometimes applied. Thus a solution containing, for example, 0.050 gram of $PO_4^{\equiv}$ ion per cubic centimeter is referred to as one having a $PO_4^{\equiv}$ ion-titre of 0.050.

3. *Per-Cent-by-Weight Solutions.*—The strength of certain solutions is sometimes designated by the per cent by weight of solute contained in the solution. Thus a solution which contains, say, 20 grams of the solute in 100 grams of the solution is a 20 per cent solution.

In practice, however, a " 20 per cent solution " is sometimes erroneously made up to contain 20 grams of the solute in 100 cc. of the solution.

4. *Designation by Means of Specific Gravity.*—The specific gravity of a solution is sometimes used to indicate the strength of a reagent solution. This system can be employed only in conjunction with the per cent by weight and necessitates the use of a specific gravity table for each kind of solution. The concentration of the common neutralization reagents, namely, HCl, H_2SO_4, HNO_3 and NH_4OH, usually is expressed by this method. Thus, the " concentrated " HCl supplied to the laboratory has a specific gravity of approximately 1.19 and contains about 37 per cent of pure HCl by weight.

5. *Normal Solutions.*—This system of concentration, extensively employed in quantitative analysis, is sometimes used in qualitative analysis to designate the strength of reagent solutions. A normal solution contains a gram-equivalent weight of the solute per liter of solution. A gram-equivalent weight is that amount of reactant which will bring into reaction, directly or indirectly, 1.008 grams of hydrogen. A normal solution of any acid therefore contains 1.008 grams of replaceable hydrogen; if the acid is monobasic, such as HCl, HNO_3 or $HC_2H_3O_2$, the molecular weight in grams will furnish the required gram-equivalent weight of hydrogen. A normal solution of H_2SO_4 contains one-half the molecular weight of H_2SO_4 in grams per liter of solution. Corresponding definitions hold for normal solutions of bases, of precipitating agents and of oxidizing and reducing agents.

6. *Molar Solutions.*—A molar solution contains the molecular weight in grams of the solute in a liter of solution. Although molar solutions are not usually employed as actual laboratory reagents, the units of concentration used, the gram-mol, or the corresponding terms gram-ion and gram-atom, are tremendously important in the mathematical treatment of all equilibria relationships.

Gram-Atom, Gram-Mol and Gram-Ion Quantities.—A gram-atom or a gram-atomic weight of an element is a weight in grams equal to the atomic weight of that element. Thus, a gram-atom of sodium consists of 22.997 grams of sodium, since this number is the atomic weight of sodium. Likewise 35.457 grams of chlorine is 1 gram-atom of chlorine, and 1.008 grams of hydrogen a gram-atom of hydrogen. One-half of the atomic weight of an

element in grams constitutes one-half of a gram-atom; one-tenth of the atomic weight in grams, a tenth of a gram-atom, etc.

A gram-mol or a gram-molecular weight (sometimes simply called a mol) is the molecular weight of a substance in grams. One gram-mol of AgCl, for example, consists of 143.337 grams of this compound, this number being the molecular weight of AgCl. A gram-mol of HCl weighs 36.465 grams, and a gram-mol of NaOH 40.005 grams. One-half of the molecular weight is a half-mol, and one-tenth of the molecular weight constitutes 0.1 of a gram-mol. Thus 0.5 of 36.465 or 18.233 grams of HCl is 0.5 of a gram-mol of HCl, and 3.647 grams of HCl is 0.1 of a gram-mol of HCl.

A gram-ion is the atomic or molecular weight of the ion in grams. That is, if the ions in a solution consist of charged *atoms,* such as Ag^+, H^+, Cl^-, etc., the atomic weight in grams of the element in question constitutes one gram-ion; and if the ions consist of *charged groups of atoms* such as the ammonium ion, NH_4^+, the nitrate, NO_3^-, the sulfate, $SO_4^{=}$, or the acetate, $C_2H_3O_2^-$, ion, the molecular weight of the charged radical, in grams, constitutes a gram-ion. If, for example, a solution of HCl contains 1.008 grams of H^+ ion and 35.457 grams of Cl^- ion, there are present 1 gram-ion of hydrogen ions and 1 gram-ion of chloride ions. Or, again, if a certain solution is made by dissolving one gram-molecular weight of $AgNO_3$ in water and the resulting solution is completely ionized into Ag^+ ions and NO_3^- ions, the solution will contain 1 gram-ion of Ag^+ ion (107.88 grams) and 1 gram-ion of NO_3^- ion (62.008 grams).

It is obvious that the three terms gram-atom, gram-mol and gram-ion are fundamentally alike and define the same kind of unit of measurement, differing only in that they refer to different conditions of matter. The gram-atom refers to the atomic state of an element, the gram-mol to a compound or uncharged radical and the gram-ion to an ionized atom or radical. This fine distinction is one of exact definition rather than of any real difference in meaning.

These units serve to express the quantity or mass of substance, and they are used in all equilibrium calculations. It is important that the student thoroughly understands the meaning of these units and how they are obtained from the usual gram weights. The conversion from gram weights to gram-atom, gram-mol or

gram-ion quantities is made by dividing the gram weight by the atomic or molecular weight:—

$$\frac{\text{Weight in grams}}{\text{Atomic or molecular weight}} = \begin{cases}\text{Gram-atom, gram-mol or} \\ \text{gram-ion quantity.}\end{cases}$$

For example, the gram-mol quantity of $AgNO_3$ represented by 16.98 grams of $AgNO_3$ is:—

$$\frac{16.98}{169.89} = 0.1 \text{ of a gram-mol.}$$

The gram-atom quantity of silver represented by 16.98 grams of $AgNO_3$ may be calculated either (1) by finding the weight of silver contained in the given weight of $AgNO_3$ and dividing this in turn by the atomic weight of Ag; or (2) more simply from the gram-mol quantity of $AgNO_3$; for, since one molecule of $AgNO_3$ contains one atom of Ag, 0.1 of a gram-mol of $AgNO_3$ contains 0.1 of a gram-atom of Ag.

Furthermore, if this quantity of $AgNO_3$ is dissolved in a sufficiently large volume of water to result in complete ionization, there would be present 0.1 of a gram-ion of Ag^+ ion.

Conversely, to convert quantities expressed in terms of gram-mol, gram-atom or gram-ion units to gram weights, multiply the quantity by the molecular or atomic weight of the molecule, atom or charged radical.

Molar and Gram-Ion Concentrations.—A molar solution has already been defined as one containing the molecular weight of the solute in grams in *1 liter of the solution.* If one-half of the molecular weight in grams of the solute is present in a liter of the solution, the concentration of the solution is said to be 0.5 molar. In the case of $AgNO_3$ previously referred to, if 0.1 of a gram-mol of $AgNO_3$ is present in a liter of the solution, the solution is 0.1 molar, with respect to the solute; we say that its molarity is 0.1.

If this $AgNO_3$ solution is completely ionized, the gram-ion concentrations of Ag^+ ion as well as of NO_3^- ion are 0.1 of a gram-ion; i.e., C_{Ag^+} is 0.1 and $C_{NO_3^-}$ is likewise 0.1.

It should be carefully noted that the terms molar concentration and gram-ion concentration refer specifically to the amount of solute, and of ions, respectively, in a liter of solution. The gram-mol and gram-ion *quantities* are identical with the molar and

gram-ion *concentrations* only when the volume of solution is 1 liter. For volumes other than a liter, the concentration remains the same but the absolute quantity will be different. Thus, if 200 cc. of a $AgNO_3$ solution containing 0.1 gram-mol of dissolved $AgNO_3$ per liter is taken, there is present only two-tenths of the amount of solute, namely, 0.02 gram-mol, but the solution is still a 0.1 molar solution.

When a solute ionizes to furnish two ions of the same kind and one of another kind, as for instance, in the case of $Ca(NO_3)_2$, which ionizes according to the scheme:

$$Ca(NO_3)_2 \rightleftharpoons Ca^{++} + 2NO_3^-$$

the gram-ion concentration of NO_3^- ion is twice that of the Ca^{++} ion.

If the solution is known to be incompletely ionized the gram-ion concentrations of the ions as well as the gram-molar concentration of that portion of the solute which is not ionized are readily found by multiplying the molarity of the solution by the degree of ionization. In the above case, suppose that a 0.1 molar solution of $Ca(NO_3)_2$ is 85 per cent ionized. The concentration of the Ca^{++} ion is then 0.1×0.85 or 0.085 gram-ion, the concentration of the NO_3^- ion is 0.2×0.85 or 0.170 gram-ion and the concentration of the non-ionized $Ca(NO_3)_2$ is 0.1×0.15 or 0.015 gram-mol.

The Calculations of Qualitative Analysis.—In the study of the fundamental theory and of the reactions of qualitative analysis, computations must frequently be made involving the concentrations of ions and non-ionized solutes, the use of various equilibrium constants, the effect of reagents, etc. In fact, the only effective way to understand thoroughly and apply properly the theoretical principles is by repeated practice and use of calculations. See in this connection, the senior author's *Calculations of Qualitative Analysis.* Equilibrium calculations of one kind or another are the most important types of computations encountered in the study of qualitative analysis. In these calculations, the data such as equilibrium constants and ionic concentrations are small numbers, and it is more convenient to express such quantities in the exponential form than as decimal fractions.

The Use of Exponents in Calculation.—The magnitude of a quantity is expressed in the exponential form by writing the digits as coefficients multiplied by 10 raised to the proper power. Thus

the number 1000, which is the product of $10 \times 10 \times 10$, or ten cubed, is written 1×10^3. The number 0.001, the product of $0.1 \times 0.1 \times 0.1$, becomes 1×10^{-3}, and 0.00001 becomes 1×10^{-5}, the significant figure, in each of the above cases 1 or unity, appearing as the coefficient, and the negative exponent being one more than the number of zeros used to locate the decimal point in the decimal fraction. When more than one significant figure appears in the number, it is conventional to place the decimal point after the first digit in the coefficient and to adjust the negative exponent accordingly. For example, 0.0000182 is written 1.82×10^{-5}.

In the operations of multiplying, dividing, squaring, cubing, extracting square and cube roots, etc., the numbers are expressed in the exponential form and the coefficients are treated in the ordinary arithmetical manner. The exponents are added algebraically for a multiplication, doubled for squaring and tripled for cubing. In a division the exponents are subtracted algebraically; in extracting a square root, the exponent is divided by 2, and for a cube root the exponent is divided by 3.

Calculations Applied to Reagents and Test Solutions.—The preparation of test solutions has already been described and illustrated for silver. Since the student's individual set of test solutions contains 1 mg. of the cation per cubic centimeter, these solutions must be made by dilution of the stock solutions. The gram-ion concentration is determined by dividing the weight in grams in 1 liter by the atomic weight of the metallic ion in question. This value then is the same, whether a liter, 10 cc., 1 cc. or one drop of the solution is under consideration. (One drop may be considered as $\frac{1}{20}$ cc.)

Another type of calculation is frequently encountered where, as in the case of the common acids, a dilute reagent is prepared from the concentrated one. Thus, for dilute HCl, the instructions call for diluting 10 cc. of the concentrated HCl with 20 cc. of water. The concentrated HCl has a specific gravity of 1.19 and contains 37.23 per cent of HCl by weight. If to this are added 20 cc. (or 20 grams) of water, the final percentage by weight can readily be determined by the relation:

$$(10 \times 1.19 \times 0.3723) + 20 = [(10 \times 1.19) + 20]x$$

where x is the final percentage of pure HCl. The specific gravity of the diluted reagent corresponding to the new percentage of HCl is then found from specific gravity tables.

Some General Remarks Regarding Reagents Used in the Procedures of Analysis.—At this point, the reagent lists for solid and liquid reagents in the appendix should be examined and checked against the student's own set. The reasons for supplying some of the reagents in solid form are that (1) certain of these substances are insoluble, (2) some give unstable solutions or are required when a freshly prepared solution is called for and (3) more intensified reactions are obtained in certain cases when the reagent is added in the solid form rather than as a solution. With regard to the liquid reagents, the following observations might profitably be made, thereby obtaining a broad perspective of the general nature and preparation of these reagents. Note that:

1. Some of the reagents are organic liquids such as ether, alcohols, chloroform, acetone, etc., while the majority are solutions.
2. Water is the most common solvent, although organic liquids are used in the preparation of a few reagents.
3. Inorganic as well as organic compounds constitute the solutes.
4. Most of the reagents are prepared by dissolving the specified amount of the solute in 100 cc. of the solution. These are therefore empirical solutions in respect to designating their strength. The " concentrated " acids, namely, HCl, H_2SO_4 and HNO_3, as well as NH_4OH, are designated by their specific gravity and percentage by weight.
5. The " dilute " acid reagents and dilute NH_4OH are prepared by the student by proper dilution of the more concentrated solution.
6. The reagent list indicates the purpose of the reagent when it is used as a final test reagent; when not so designated, the reagents find their proper use throughout the procedures of analysis.

Reactions

The study of the reactions encountered in the procedures of qualitative analysis constitutes one of the most important parts of the student's work since naturally the methods of separation and identification are based on suitably selected reactions. Reactions, to be of the greatest service in bringing about sharp separations and distinctive tests, should go practically to completion. In aqueous solutions, reactions are ionic and reach an equilibrium;

consequently those reactions in which equilibrium is reached only when the reaction has run far to completion are the most serviceable ones. The ionic reactions with which we are concerned in qualitative analysis are of only two fundamentally different types, namely:

1. Those which take place because ions combine.
2. Those which take place because electrons are transferred.

The reactions of the first type may be further subdivided into several kinds depending upon the nature of the product formed. Ions may combine because:

(*a*) A less ionized acid or base (in rare cases a less ionized salt) forms. Neutralization and hydrolysis reactions are examples of this kind.

(*b*) A precipitate forms.

(*c*) A complex ion is produced in the solution.

(*d*) A gas is liberated.

(*e*) The concentration of an amphoteric ion is altered.

Reactions of the second type, in which electrons are transferred, are the oxidation-reduction reactions. Further reference is made to this important type in connection with balancing equations of this kind.

The equilibrium relationships based on this classification of ionic reactions constitute the most important part of the study of the fundamental principles discussed in the following sections.

The Writing and Balancing of Chemical Equations.—The writing of equations and the ability to balance them correctly must be acquired before any intelligent progress can be made in the study of analytical chemistry. A chemical equation cannot be written and balanced unless the reactants and products are known. What takes place in a reaction must be discovered by experiment. The equation must represent what actually takes place.

If the formulas of the compounds or ions involved are known, it is usually a comparatively simple matter to balance the coefficients. A great many equations can be balanced by inspection. Where the actions are more complicated, writing the reactions in steps and canceling out the members that are common to the two successive reactions will usually result in a correctly balanced

final equation. Special consideration is given in a later section to oxidation-reduction reactions, which usually cause the greatest difficulty in balancing.

Inasmuch as most of the reactions with which we are concerned are between ions, the equations representing such reactions are written as ionic equations. The complete form of setting up such interactions is discussed on page 27. In the remainder of the book, the simple ionic form will be used, showing only those ions and products which are mainly involved in the reactions. Sometimes reactions will be given in molecular form, whenever such chemical changes can be more clearly comprehended and the chemical relationships better shown; it must be understood, however, that ionic interchange always takes place even though for the sake of clearness the reaction may be expressed in molecular form.

Ionic reactions which lead to the formation of precipitates, of less ionized products, of gases and of complex amphoteric ions are, as previously noted, usually easy to balance, the selection of the correct coefficients being ordinarily a matter of simple inspection. More difficulty is usually encountered by the student with the equations representing oxidation-reduction reactions.

The Electric Charges of the Ions.—Some of the aspects of the phenomenon of ionization and the factors which influence its extent having been considered, the source of the electric charges with which the ions are endowed will now be briefly discussed. Our present conception of the structure of atoms is that they consist of an inner nucleus made up of a combination of positive units of electricity called protons and negative units called electrons, this nucleus being surrounded by one or more shells containing electrons, the atom as a whole being electrically neutral. The nucleus always contains an excess of positive units and is therefore positively charged, and the external shells must contain enough electrons to compensate for this. Thus the hydrogen atom has one proton as its nucleus and one electron in its shell. The helium atom contains in its nucleus four protons and two electrons; its shell must contain two electrons. An atom which loses electrons becomes positively charged, and one which gains electrons becomes negatively charged. Thus for the hydrogen atom, when it loses its electron, the residue, consisting of only the nucleus, is positively charged. The sodium atom tends to lose one electron from its outermost shell, leaving a net charge of +1. Zinc loses two and

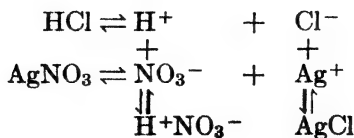
aluminum three electrons, leaving net charges of $+2$ and $+3$, respectively. Atoms like that of fluorine or chlorine readily gain an electron to give the atom its most stable configuration, with a net charge of -1.

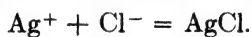
When, for example, a neutral atom of sodium reacts with a neutral atom of chlorine, the sodium loses one electron which is taken up by the chlorine and there is produced a molecule of sodium chloride in which the sodium is positively charged and the chlorine negatively charged. When such a compound is dissolved in water, the attraction between the atoms is more or less weakened, the molecules dissociate more or less completely and the charged atoms or radicals become free and independent units, namely, the cations and anions. In an ionizing medium the charged radicals are then most capable of producing chemical reactions.

Ionic Nature of Reactions.—Since most of the reactions of qualitative analysis take place in aqueous solutions of electrolytes, the actual chemical changes involved must be considered as taking place between ions and not between the non-ionized components of the solute. In other words, we are concerned almost entirely with ionic reactions, and the most general application which we can make of the theory of ionization is that the chemical changes are ionic in nature. The reactions must, therefore, be represented as ionic equations, and not in molecular form. An example will make this clear. Suppose we take a solution of $AgNO_3$ and add to it dilute HCl. A curdy white precipitate of AgCl will at once form. The same result can be obtained by mixing a solution of NaCl, NH_4Cl, $BaCl_2$ or other soluble chloride with the solution of any soluble silver salt. If the reaction were expressed in molecular form, as:

$$HCl + AgNO_3 = AgCl + HNO_3$$

it would imply reaction between molecules. But we have sufficient evidence supporting the theory of ionization that dilute solutions of $AgNO_3$, HCl, NaCl, etc., are highly dissociated into their respective ions. The complete form in which reactions of this kind are represented is:

$$\begin{array}{rlcl}
HCl \rightleftharpoons & H^+ & + & Cl^- \\
 & + & & + \\
AgNO_3 \rightleftharpoons & NO_3^- & + & Ag^+ \\
 & \downarrow\uparrow & & \downarrow\uparrow \\
 & H^+NO_3^- & & \underline{AgCl}
\end{array}$$

The products formed by this double decomposition result from an interchange of ions of the original solutions. The fact that one of the products, nitric acid, is highly ionized is indicated by placing the proper charges on the atoms of the molecule, and being highly ionized, there will be little tendency towards its formation. The other product, silver chloride, is only slightly soluble in the mixed solutions, a fact indicated by underscoring its formula. Silver ions and chloride ions are thus removed in the form of an insoluble precipitate causing the reaction to go practically to completion. These are the ions that are mainly affected in this reaction, and for simplicity we can express the change as a simple ionic reaction:

$$Ag^+ + Cl^- = \underline{AgCl}.$$

The student must early acquire this ionic point of view and consider all reactions, with but few exceptions, as taking place between the ions concerned.

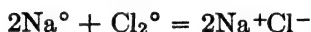
The Nature of Oxidation and Reduction.—Oxidation and reduction depend upon valence changes. If an atom is oxidized its positive valence is increased or its negative valence decreased; when a reduction takes place, the atom of the element concerned suffers a decrease in positive valence or an increase in negative valence. We must therefore look to the elements of variable valence for the more commonly occurring cases of oxidation and reduction, but we must also remember that the conversion of an element from a condition of zero valence to any other valence state, or vice versa, involves either an oxidation or a reduction.

The valence of an element is usually indicated by attaching to its symbol the proper number of positive or negative charges. By writing the formula of the oxidizing or reducing agent, and inserting the proper number of charges, the valence condition of the element which is capable of change can usually be ascertained.

We have already considered (page 26) the source of the charges on the ions and have seen that when a neutral atom loses electrons from its outer shell it becomes a positively charged ion (cation), and when other neutral atoms or groups of atoms gain electrons they become negatively charged ions (anions), and that in a chemical compound, which is electrically neutral, the charged atoms are held together by mutual attraction. The sum of positive charges must equal the sum of negative charges in a molecule, and in an ionizing solvent the molecules of the solute are more or

less broken down into their constituent ions, the solution being of course electrically neutral.

Thus, when metallic sodium reacts with water, the neutral sodium atom loses one electron and becomes an ion (Na^+) with a net charge of +1. When zinc is dissolved in sulfuric acid, the zinc atom loses two electrons and becomes a cation with a net charge of +2. The diatomic chlorine molecule, on the other hand, when changed from the molecular to the ionic state, accepts, for each atom, one electron, giving rise to two ions each with a −1 charge. If sodium is burned in chlorine, the reaction takes place:

$$2Na^\circ + Cl_2^\circ = 2Na^+Cl^-$$

yielding one molecule of NaCl for each atom of sodium and chlorine used up. The electron lost by the sodium is taken up by the chlorine atom.

The number of chlorine or hydrogen atoms taken up or replaced by an atom of an element is spoken of as the valence of that element. Thus in the above reaction the valence of sodium is 1. In terms of the electron theory, however, **valence is defined as the number of electrons lost or gained by an atom of an element when it combines with or replaces atoms of another element.** Thus hydrogen, sodium and potassium, for example, are univalent, because the atom loses one electron on becoming an ion. Chlorine and bromine gain one electron on becoming chloride and bromide ions and in this form are univalent. Zinc and calcium are examples of bivalent elements and aluminum of a trivalent element. Many elements exhibit more than one valence state under different conditions, the valence number being determined by the number of electrons lost or gained in the particular reaction concerned.

Oxidation and Reduction in Terms of Valence and Electron Transfer.—The old and limited meaning, that oxidation involves the direct addition of oxygen or chlorine or similar element and reduction involves the addition of hydrogen or loss of oxygen, must be replaced, in the light of modern chemistry, by a broader conception. Since, when an element is oxidized its positive valence is increased, and when it is reduced its positive valence is decreased, we can define **oxidation as an increase in positive valence or a decrease in negative valence and reduction as an increase in negative valence or a decrease in positive valence.**

Moreover, since the valence of an element is defined as the number of electrons lost or gained by a neutral atom, the term oxidation means a decrease in the number of electrons associated with the atom. Reduction, likewise, in terms of electrons, means a gain in the number of electrons by an atom. **In the broadest sense, then, oxidation means the loss of one or more electrons and reduction the gain of one or more electrons.** In every reaction in which there is a transfer of electrons from one kind of atom to another, the electrons lost by atoms of one element must be gained by atoms of another element. That is, when one substance is oxidized, another substance is reduced. Thus, in the reaction of metallic zinc with sulfuric acid, according to the molecular equation:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

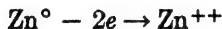
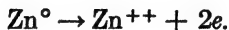
the change of valence is shown by writing the equation in ionic form:

$$Zn^\circ + 2H^+ = Zn^{++} + H_2^\circ$$

in which the neutral atom of zinc with zero valence becomes oxidized to the divalent positively charged zinc ion, while two hydrogen ions are reduced to zero valence, becoming a molecule of gaseous hydrogen. To express the same change in terms of electrons transferred, use is made of partial or " half-cell " equations which show the changes undergone by each reactant in the reaction. Thus, in the above reaction, the neutral atom of zinc, on being oxidized to the divalent Zn^{++} ion, loses two electrons, that is, two electrons ($2e$) are products of the change of the zinc atom, and we express this either in the form:

$$Zn^\circ - 2e \rightarrow Zn^{++}$$

or preferably

$$Zn^\circ \rightarrow Zn^{++} + 2e.$$

The two electrons lost by the zinc are transferred to two hydrogen ions:

$$2H^+ + 2e \rightarrow H_2^\circ.$$

For an element to function as a good oxidizing agent it must readily accept electrons from the reducing agent; and, for an

element to be a good reducing agent, it must readily part with one or more of its electrons.

When the reaction takes place by mixing solutions of the oxidizing and reducing agent, the electrons are transferred, directly in the solution, from the reducing agent to the oxidizing agent. If, however, the oxidizing agent is placed in one vessel and the reducing agent in another, the vessels joined by means of a U-tube filled with a salt solution, a strip of platinum as electrode placed in each vessel and the electrodes connected by wires through a galvanometer or voltmeter, electrons will flow through the wire from the reducing solution to the oxidizing solution. This arrangement constitutes a voltaic cell, the two vessels with their electrodes being known as half-cells. The electrical instrument will indicate an electrical current, and chemical tests will show, after an interval of time, that the reducing agent has become oxidized whereas the oxidizing agent has been reduced. By use of such electrolytic cells, the changes undergone by the oxidizing and reducing agents can be separated into the reactions taking place, individually, in the two half-cells. Such half-cell reactions, when expressed as partial equations, as illustrated above for zinc and hydrogen, enable one to study oxidation-reduction reactions more readily, as well as to balance the equations most easily. The electrochemical theory of oxidation and reduction is briefly discussed later in Part I of this book.

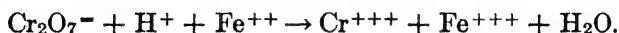
The Balancing of Oxidation-Reduction Equations.—Since a transfer of electrons takes place in an oxidation-reduction reaction, such an action should be made evident in the mechanism of balancing the equation. There are two "electron transfer" methods by which such equations may be balanced, known as the **valence-electron** method and the **ion-electron** method, respectively. These two electron transfer methods are discussed and illustrated below.

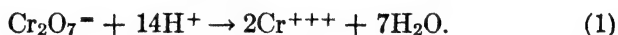
Before these two electron transfer methods are discussed, however, it will be well to consider, from a purely valence-change viewpoint, a typical oxidation-reduction reaction. In the reaction between ferrous chloride and potassium dichromate in a solution acidified with dilute HCl, the iron is oxidized from the ferrous or divalent to the ferric or trivalent condition, while the chromium in the potassium dichromate is reduced from the hexavalent state to the chromic or trivalent condition, the oxygen of the dichromate

uniting with the hydrogen of the acid to form water. This reaction in unbalanced, molecular form is:

$$K_2Cr_2O_7 + HCl + FeCl_2 \rightarrow CrCl_3 + FeCl_3 + H_2O + KCl.$$

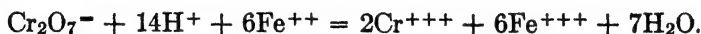
Rewriting this equation in ionic form, to include only the essential components involved, gives:

$$Cr_2O_7^{=} + H^+ + Fe^{++} \rightarrow Cr^{+++} + Fe^{+++} + H_2O.$$

The chromium atom in the dichromate radical has an apparent valence of $+6$; in the chromic state it has a valence of $+3$; each chromium atom suffers a reduction of three positive valences. Since there are two atoms of chromium in each dichromate ion, each atom of which loses three positive charges, the total loss will be six for each dichromate radical. The seven oxygen atoms require fourteen hydrogen ions for $7H_2O$. The changes with respect to the oxidizing agent can therefore be expressed by the equation:

$$Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O. \qquad (1)$$

The six charges lost by one $Cr_2O_7^{=}$ ion must be accounted for by the gain of six positive charges on the iron. Since each ferrous ion shows an increase of one positive valence on becoming a ferric ion, the six units from one dichromate ion are assumed by six ferrous ions. The changes with respect to the reducing agent are therefore:

$$6Fe^{++} \rightarrow 6Fe^{+++}. \qquad (2)$$

Adding equations (1) and (2) gives the completed equation in ionic form:

$$Cr_2O_7^{=} + 14H^+ + 6Fe^{++} = 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

To rewrite this in the original molecular form, account must be taken of the potassium and chloride ions. The $2K^+$ ions associated with $K_2Cr_2O_7$ now may be considered to be associated with $2Cl^-$ ions to form 2KCl. The fourteen Cl^- ions from the HCl and twelve Cl^- ions from $6FeCl_2$ supply those needed by $2CrCl_3$, $6FeCl_3$ and 2KCl. The final, molecular equation then is:

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 2CrCl_3 + 6FeCl_3 + 7H_2O + 2KCl.$$

The Valence-Electron Method.—In this method the number of electrons given up by the reducing agent and those gained by

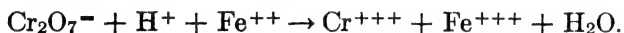
the oxidizing agent are determined by the actual valence changes undergone by the atom in the reducing and oxidizing compound, element or ion. The method must be used in reactions in which molecules react, i.e., in truly molecular reactions, but may also advantageously be applied to ionic reactions in which there is no doubt or difficulty in ascertaining the valence change of the atom in question.

As an example we may take the above reaction between ferrous chloride and an acidified solution of $K_2Cr_2O_7$.

The reaction in molecular, unbalanced form is written:

$$K_2Cr_2O_7 + HCl + FeCl_2 \rightarrow CrCl_3 + FeCl_3 + KCl + H_2O.$$

Rewriting this in ionic form, to show the essential changes undergone by the ions, gives:

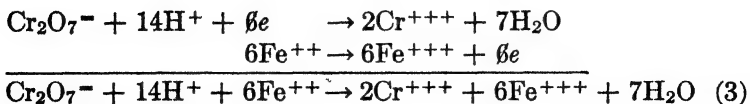
$$Cr_2O_7^{=} + H^+ + Fe^{++} \rightarrow Cr^{+++} + Fe^{+++} + H_2O.$$

In the dichromate ion, $Cr_2O_7^{=}$, each chromium atom has a valence of +6; the chromic ion, Cr^{+++}, consists of a chromium atom with +3 charges. Each chromium atom loses +3 charges, which, for the two atoms in the dichromate ion, means a gain of 6 electrons. The oxygens unite with the hydrogen ions to produce water. The half-cell reaction for the oxidizing agent can now be expressed by the equation:

$$Cr_2O_7^{=} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O. \quad (1)$$

In like manner, the ferrous ion of the reducing agent becomes oxidized to the ferric state, undergoing a valence change from +2 to +3. This is the result of the loss of one electron by each ferrous ion. The change may be expressed by the equation:

$$Fe^{++} \rightarrow Fe^{+++} + 1e. \quad (2)$$

The electrons required for the reduction of the dichromate ion are supplied by the ferrous ions, and, to fulfill this requirement, six ferrous ions are required. The two half-cell reactions may now be added:

$$\begin{array}{l} Cr_2O_7^{=} + 14H^+ + \cancel{6e} \rightarrow 2Cr^{+++} + 7H_2O \\ \qquad\qquad\qquad 6Fe^{++} \rightarrow 6Fe^{+++} + \cancel{6e} \\ \hline Cr_2O_7^{=} + 14H^+ + 6Fe^{++} \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O \quad (3) \end{array}$$

equation (3) giving the balanced ionic equation.

This ionic equation may easily be transformed into the molecular one:

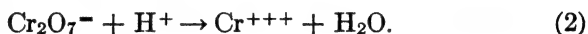
$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 \rightarrow 2CrCl_3 + 6FeCl_3 + 7H_2O + 2KCl.$$

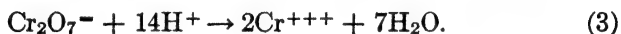
The Ion-Electron Method.—In this method, which can be applied only to ionic reactions, the electrons are balanced on the basis of changes in the charges on the ions, and not on the charges of the element contained in the ion. The dichromate-ferrous reaction may again be taken as an example.

Writing the reaction in ionic form:

$$(Cr_2O_7)^{=} + H^+ + Fe^{++} \rightarrow Cr^{+++} + Fe^{+++} + H_2O \qquad (1)$$

shows that the $(Cr_2O_7)^{=}$ ion is reduced to the chromic ion, Cr^{+++}. The unbalanced half-cell equation for this is:

$$Cr_2O_7^{=} + H^+ \rightarrow Cr^{+++} + H_2O. \qquad (2)$$

To first balance this chemically requires $14H^+$ to unite with 7O forming $7H_2O$, and Cr_2 becomes $2Cr^{+++}$:

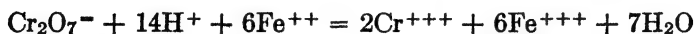
$$Cr_2O_7^{=} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O. \qquad (3)$$

The electrical balance between positive and negative charges is next obtained in order to ascertain the number of electrons required. There are 14+ charges and 2− charges on the left and 6+ charges on the right; consequently 6− charges are required. The 6− charges are supplied by 6 electrons:

$$Cr_2O_7^{=} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O. \qquad (4)$$

Each ferrous ion liberates one electron, therefore the half-cell reaction for the iron is:

$$6Fe^{++} \rightarrow 6Fe^{+++} + 6e.$$

Adding (4) and (5) gives the completed ionic equation:

$$Cr_2O_7^{=} + 14H^+ + 6Fe^{++} = 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$

and the molecular equation is as before:

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 2CrCl_3 + 6FeCl_3 + 7H_2O + 2KCl.$$

Oxidizing and Reducing Agents.—Many desired changes are brought about in qualitative analysis through the addition of oxidizing or reducing reagents; therefore the study of oxidation-

reduction reactions is of considerable importance. The oxidizing agents most frequently used are nitric acid, aqua regia, chlorine, hydrogen peroxide, sodium peroxide, potassium chlorate, potassium permanganate and potassium dichromate. See Table III. The commonest reducing agents which are employed in qualitative analysis are stannous chloride, ferrous salts, hydrogen sulfide, sodium sulfite, potassium iodide and metals. Table IV gives a more complete list of reducing agents. Suitable pairs must of course be selected to cause the specific reaction to run practically to completion, since the ease of electron interchange varies widely for different substances. Proper conditions of acidity or alkalinity must also be established in the solution.

TABLE III

COMMON OXIDIZING AGENTS

Compound Used	Element or Radical Involved	Apparent Valence of Element	Reduced to	New Valence	Decrease in Valence	Gain in Electrons per Atom
Cl_2	Cl	0	Cl^-	−1	1	1
Br_2	Br	0	Br^-	−1	1	1
I_2	I	0	I^-	−1	1	1
NaOCl	OCl^-	+1	Cl^-	−1	2	2
$KClO_3 + HCl$	Cl (as Cl_2)	0	Cl^-	−1	1	1
Aqua regia	Cl (as Cl_2)	0	Cl^-	−1	1	1
HNO_3 (dilute)	N	+5	NO	+2	3	3
HNO_3 (conc.)	N	+5	NO_2	+4	1	1
Na_2O_2	O	0	O^{--}	−2	1	1
H_2O_2	O	0	O^{--}	−2	1	1
PbO_2	Pb	+4	Pb^{++}	+2	2	2
$KMnO_4$ (acid)	MnO_4^-	+7	Mn^{++}	+2	5	5
$KMnO_4$ (basic)	MnO_4^-	+7	MnO_2	+4	3	3
$K_2Cr_2O_7$ (acid)	$Cr_2O_7^{--}$	+6	Cr^{+++}	+3	3	3
K_2CrO_4 (basic)	CrO_4^{--}	+6	Cr^{+++}	+3	3	3

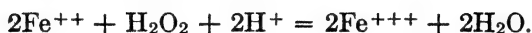
Some comment on these oxidizing agents is necessary. The free halogens (Cl_2, Br_2, I_2) owe their oxidizing ability to the ease with which they accept electrons, becoming thereby negatively charged ions. In hypochlorites (ClO^-) and chlorates (ClO_3^-) the chlorine atom has charges of +1 and +5, respectively, and on

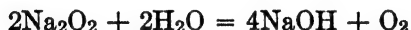
being reduced to chloride the decrease in valence (gain in electrons) is 2 and 6, respectively. Aqua regia, three parts of concentrated HCl to one part of concentrated HNO_3, is a very powerful oxidizing solvent, owing to the free chlorine which is liberated in the reaction:

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O.$$

Nitric acid is very often used as an oxidizing solvent, as, for example, to dissolve metals and sulfides. It is most commonly reduced to NO, the nitrogen going from a valence of +5 to a valence of +2. The extent of reduction depends upon the concentration of the nitric acid as well as upon the nature and strength of the reducing agent. In very concentrated nitric acid solutions, the reduction is only to NO_2.

Hydrogen peroxide, H_2O_2, may act either as an oxidizing or as a reducing agent. Its structural formula may best be written thus $H^+ - {}^-O^+ - {}^-O^- - H^+$, and when decomposed yields an atom of oxygen. When acting as an oxidizing agent the neutral atom, ${}^-O^+$, is reduced to ${}^-O^-$, thus undergoing a valence change from zero to -2, i.e., gaining two electrons, and water is formed as one of the products of the reaction. Thus elements in the reduced state are oxidized, as, for instance:

$$2Fe^{++} + H_2O_2 + 2H^+ = 2Fe^{+++} + 2H_2O.$$

Sodium peroxide owes its strong oxidizing nature to the liberation of oxygen by its reaction with water:

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

the oxygen atom functioning in the same manner as that in hydrogen peroxide mentioned above.

Potassium permanganate when in acid solution is reduced to manganous ion, Mn^{++}, the valence of the manganese atom going from +7 to +2, thus suffering a loss of five units (a gain of five electrons). In neutral or basic solution, however, the manganese in the permanganate ion is reduced only to the tetravalent condition, forming, as a general rule, MnO_2. Here the gain of electrons is only three instead of five.

In dichromates and in chromates the valence of the chromium

atom is 6. The form of the ion present is solely dependent upon the acidity of the solution as can be seen from the reactions:

$$Cr_2O_7^{=} + 2OH^- \rightleftharpoons 2CrO_4^{=} + H_2O$$

and

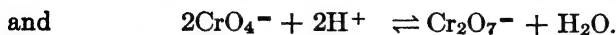
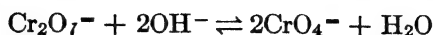
$$2CrO_4^{=} + 2H^+ \rightleftharpoons Cr_2O_7^{=} + H_2O.$$

Hence in basic solution the chromate ion predominates; in acidic solution the dichromate ion predominates.

Table IV shows a number of frequently used reducing agents, the proper selection of which of course depends upon the substance to be reduced and the conditions under which the reaction takes place. Ferrous salts and stannous salts are readily oxidized to the ferric and stannic condition. Sulfurous acid is an effective reducing agent, introduced usually by adding Na_2SO_3 to the moderately acidified solution to be reduced. Hydrogen sulfide reduces many substances, such as the halogens, nitric acid, dichromates, permanganates, etc., with the liberation of free sulfur, a circumstance which cannot be overlooked when using H_2S as a precipitating agent.

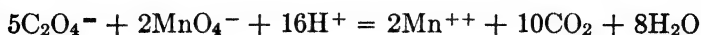
TABLE IV

COMMON REDUCING AGENTS

Compound Used	Element or Radical Involved	Apparent Valence of Element	Oxidized to	New Valence	Increase in Valence	Loss of Electrons per Atom
$FeSO_4$	Fe^{++}	+2	Fe^{+++}	+3	1	1
$SnCl_2$	Sn^{++}	+2	Sn^{++++}	+4	2	2
H_2S	$S^{=}$	−2	S°	0	2	2
H_2S	$S^{=}$	−2	$SO_4^{=}$	+6	8	8
Na_2SO_3	$SO_3^{=}$	+4	$SO_4^{=}$	+6	2	2
Na_3AsO_3	$AsO_3^{\equiv}$	+3	$AsO_4^{\equiv}$	+5	2	2
$H_2C_2O_4$	$C_2O_4^{=}$	(+3)	CO_2	+4	1	1
KI	I^-	−1	I_2°	0	1	1
H_2O_2	O	−2	O_2°	0	1	1
Metals, e.g., Zn	Zn	0	Zn^{++}	+2	2	2
Hydrogen	H_2	0	H^+	+1	1	1

In oxalic acid, which is oxidized to CO_2 and water in oxidation-

reduction reactions, as, for instance, in the reduction of permanganate:

$$5C_2O_4^{=} + 2MnO_4^{-} + 16H^{+} = 2Mn^{++} + 10CO_2 + 8H_2O$$

the two carbon atoms have different valences, and the apparent total change in valence is 2 for one molecule of oxalic acid.

General Considerations Regarding the Reactions Involved in the Procedures of Analysis.—Since the reactions employed in the processes of analysis take place, practically always, between the test substances and the added reagents, the function of the reagent and the kind of a reaction it produces should be carefully and consistently noted by the student. He should, of course, keep a laboratory record book in which the results and observations of his experiments are recorded together with the equations for the reactions involved. By carrying out the suggested experiments with test substances, taken singly and in groups, he gradually acquires the necessary fund of chemical facts upon which the theory is based and by which a successful analysis can be carried out. The final procedures of analysis are developed through the selection of reactions by which the ions are separated, isolated and finally identified. By classifying the reactions, as he progresses through the preliminary work in the study of the properties of the cations and anions (before systematic analysis is undertaken), the student will discover for himself that the general purpose of the reaction is either to separate the ion in question or to use it as a final test, and further, that:

1. More than half of the reactions employed are reactions of precipitation.
2. A considerable number are oxidation-reduction reactions.
3. Some result in the formation of amphoteric forms, complex ions, neutralizations, products of hydrolysis, evolution of gases, etc.
4. In still other reactions, colored adsorption compounds, " lakes " and complex organic compounds are produced.

Furthermore, a considerable number of the reactions embraced in 2 and 3 above are employed in dissolving precipitates and residues. In fact, the reactions by which ions are separated are almost exclusively those of precipitation and dissolving, accompanied, at times, by an oxidation or reduction, a neutralization or similar secondary effect.

On account of the frequency with which oxidations and reductions are encountered in the procedures of analysis, special reference to these reactions should be helpful at this point. In the first place it should be remembered that many of the test cations and anions are either oxidizing or reducing in their tendency. For example, Sn^{++}, Fe^{++}, $AsO_3^{\equiv}$, I^-, Br^-, $SO_3^{=}$, $S_2O_3^{=}$, $S^{=}$, $C_2O_4^{=}$, CN^-, etc., are strong reducing ions whereas, on the other hand, such ions as Fe^{+++}, $AsO_4^{\equiv}$, $CrO_4^{=}$, MnO_4^-, etc., are strongly oxidizing. Ions of this kind become oxidized or reduced by the addition, to the solution, of oxidizing or reducing agents. In the second place, the addition of an oxidizing or a reducing reagent may be either for the express purpose of causing a desired oxidation or reduction, or, on the other hand, it may be for some other reason, the accompanying oxidation or reduction being merely an incidental effect. For example, stannous chloride is utilized as a reducing agent in the test for mercury; bromine is employed to oxidize the iron to the ferric condition; $KMnO_4$, to oxidize the oxalate ion, etc. But, H_2S, for example, used as a precipitating agent, will also act as a reducing agent towards any oxidizing ions present in the solution, and HNO_3 used as a solvent will also function as an oxidizing agent.

REACTION VELOCITY, MASS ACTION AND THE LAW OF CHEMICAL EQUILIBRIUM

Reaction Velocity

The speed with which chemical changes take place varies widely for different reacting substances. Thus the rusting of iron at ordinary temperatures is a comparatively slow reaction, but many other reactions take place practically instantaneously. By reaction velocity is meant the amount of reactant transformed in unit time. Reaction velocities can be measured experimentally by determining the amount of substance which is used up or formed during definite intervals of time under definite, specified conditions. For the same reacting substances the velocity of reaction depends upon such factors as temperature, pressure and the concentration of each. Increase in temperature speeds up all reactions, the velocity being about doubled for every 10° C. rise in temperature. The influence of changes in temperature and pres-

sure on a reacting system which has come to equilibrium will be taken up later.

The amount of substance present and capable of reacting is a very important factor influencing reaction velocity. The effect of the concentration of the reacting components on the speed of the reaction, called mass action, is of fundamental importance in the study of chemical changes.

Mass Action

The substances undergoing change in a reaction are known as the **active masses** or the concentrations, the actual quantity being expressed in gram-mols or gram-ions. The amount of substance transformed in unit time depends upon the amount of each reactant present, temperature and other factors remaining constant. Doubling the amount of one reactant will necessarily result in more being transformed into the products of the reaction. The effect of the mass on the reaction velocity is called **mass action,** and the generalization which follows from this can be stated thus: **The velocity of a reaction is proportional to the active masses present at any instant.** Suppose a given number of molecules of the substance A to be reacting with a like number of molecules of B. The rule states that the rate at which A will react with B is proportional to the amounts of A and B present. The reaction velocity will therefore be equal to the product of the molar concentrations of A and B times a proportionality factor, k (velocity constant), characteristic of this particular reaction. Algebraically this can be represented thus:

Reaction velocity = Molar concentration of $A \times$ Molar concentration of $B \times k$.

Or, more simply, if we let C stand for the molar concentration of any particular reacting component and v for the reaction velocity:

$$v = C_A \times C_B \times k.$$

If two molecules of A react with one of B the expression becomes:

$$v = C_A \times C_A \times C_B \times k$$

or, squaring the concentration of A:

$$v = (C_A)^2 \times C_B \times k.$$

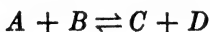
In general, if n mols of A react with m mols of B the general velocity equation is expressed thus:

$$v = (C_A)^n \times (C_B)^m \times k$$

the total molar concentration of each component being raised to a power equal to the coefficient representing the number of like reacting parts.

Reversibility of Reactions.—The extent to which a reaction will proceed in one direction depends, among other factors, upon the nature of the products formed. If the newly formed products show any tendency to interact among themselves to re-form the initial reactants an opposing action will be set up in the reverse direction, and the net effect is that the entire amount of the initial components is not transformed when the reaction appears to stop. Some reactions show marked tendency to reverse—so marked that they are of little value in analytical chemistry. In other reactions, reversibility is less pronounced, and here the reactions run nearly, but *not entirely*, to completion. These are the analytically useful ones as will be emphasized later. **All reactions are reversible to a certain extent.** This point cannot be overemphasized because it is the basis upon which our fundamental theory rests.

Equilibrium.—In all reacting systems, therefore, a condition will be reached where a certain, even though small, concentration of the initial reactants can exist side by side with the products of the reaction without further change apparently taking place. A state of equilibrium is set up. It is a dynamic equilibrium and means that for any reversible reaction such as:

$$A + B \rightleftharpoons C + D$$

when equilibrium has been reached, the reactants A and B are reacting to form C and D at exactly the same rate that C and D are reacting to form A and B. Equilibria are set up in all sorts of reacting systems; for example, between gases, between dissolved molecules and their ions, between precipitates and the solution that surrounds them, between substances distributed between two solvents, etc. The fundamental law which gives expression to the state of equilibrium is called the Law of Chemical Equilibrium and is of extreme importance in the study of reac-

tions. The theory of reactions is based on this law, and it is the most fundamental principle with which we shall have to deal.

The Law of Chemical Equilibrium

In considering the reaction between A and B, we derived the algebraic expression for the reaction velocity, namely,

$$v_1 = C_A \times C_B \times k_1$$

where C stands for the molar concentrations and k_1 is a velocity constant characteristic of the reaction between A and B. Suppose we apply a similar expression to another set of reacting substances, say to C and D. This will be characterized by a different velocity, v_2, and a different velocity constant, k_2:

$$v_2 = C_C \times C_D \times k_2.$$

Now suppose that the substances C and D are the identical products resulting from A and B, and vice versa, A and B are the products resulting from C and D as in the reversible reaction:

$$A + B \rightleftharpoons C + D.$$

Hence C and D are forming during the reaction at a rate dependent upon the amounts of A and B present. As A and B are used up their masses decrease and the reaction velocity in the direction of C and D decreases. But the amounts of C and D are continually increasing and will interact to re-form A and B. When the amounts of C and D are in such proportions as to cause the reaction to reverse at the same rate that it is proceeding forward, a dynamic state of equilibrium is set up, as indicated previously. The velocities are then equal in both directions. We can then apply the velocity equations to a reaction going in both directions at the point where the concentrations are in such proportions as to make the velocity forward equal to the velocity backward. If the two algebraic equations which express the relation between velocity and concentration are equated, we have:

$$v_1 = C_A \times C_B \times k_1 = v_2 = C_C \times C_D \times k_2.$$

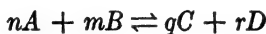
Therefore, $C_A \times C_B \times k_1 = C_C \times C_D \times k_2$, and dividing by $C_A \times C_B$ and transferring k_2, the equilibrium ratio is obtained:

$$\frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2}.$$

The ratio of the products of the molar concentrations is then equal to the ratio of the velocity constants, when equilibrium is reached. The ratio k_1/k_2 can be designated "K," which then becomes an equilibrium constant characteristic of this reaction. The equilibrium expression then is written:

$$\frac{C_C \times C_D}{C_A \times C_B} = K \quad \text{(Equilibrium constant).}$$

If for every molecule or ion of B, two molecules or ions of A are required, the value of C_A is squared in the above expression; if three times, the value is cubed, and for the general reaction:

$$nA + mB \rightleftharpoons qC + rD$$

the most general expression for the equilibrium can be written:

$$\frac{(C_C)^q \times (C_D)^r}{(C_A)^n \times (C_B)^m} = K.$$

The above expression states: **In a reacting system, at constant temperature, when equilibrium is reached, the product of the molar concentrations of the products of the reaction divided by the product of the molar concentrations of the reactants (each concentration raised to a power equal to the coefficient representing the number of like reacting parts which enter into the reaction) is always equal to a constant. This is the Law of Chemical Equilibrium.** The expression given is in the most general form. It will take on modified forms in the several applications which follow. For each reaction for which the law strictly holds, at constant temperature, the numerical value of the equilibrium constant is always the same. No matter how much the concentration of any one component in the reaction mixture varies, the proportions of the other components must change until equilibrium is again established and the value of K restored. Thus, if the

amount of A is increased in the above reversible reaction, the reaction will run faster in the direction of the formation of C and D, more of these products will be formed, the reaction will reverse at a faster rate than originally and again equilibrium will be established, with the proportions A, B, C and D changed but the ratio of the products of their molar concentrations still the same.

If the pressure on a system in equilibrium is increased, there will be a change in the proportions of the reacting components when the new equilibrium is established at the higher pressure. Of the two opposing reactions, that one will be favored which leads to a reduction in the volume of the system. This is particularly significant in gaseous reactions. There is thus a shift or displacement in the equilibrium concentrations, the system coming to equilibrium with different proportions of the reacting components.

When the temperature of a reacting system in equilibrium is changed, there is a change in the value of the equilibrium constant. That is, a new ratio is established for the equilibrium concentrations at the new temperature. With a rise in temperature, the equilibrium is shifted in the direction of the reaction which absorbs heat. The system as a whole tends to oppose the effect of the added stress placed on it; it does this by favoring that reaction which uses up the heat supplied in raising the temperature.

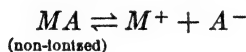
The effect of changes in concentration, pressure and temperature on a system in equilibrium is summed up in a very general law known as Le Chatelier's Law, which states: **Whenever a stress is applied to a system in equilibrium, that reaction will be favored which tends to offset or annul the effect of the stress.** Thus increasing the concentration of one component causes the reaction to proceed faster in order to lower this concentration. Increased pressure will be opposed by that reaction which tends to relieve the pressure by reducing the volume. Raising the temperature favors the reaction which, by absorbing heat, tends to lower the temperature.

The Law of Chemical Equilibrium is of wide application to a great variety of reactions. It was first shown to hold for reactions between molecules of organic substances. It is also applied to molecular gas reactions. In the reactions of qualitative analysis a number of important ionic equilibria are encountered. These

equilibria are discussed in the following sections. They will be taken up in the following order:

1. Ionization Equilibria (Ionization Constants).
2. Equilibria of Ions of Precipitates (Solubility Product Constants).
3. Hydrolysis Equilibria (Hydrolysis Constants).
4. Amphoteric Equilibria.
5. Gaseous-Liquid and Liquid-Liquid Equilibria.
6. Oxidation-Reduction Equilibria.

THE EQUILIBRIUM LAW APPLIED TO IONIZATION: IONIZATION CONSTANTS

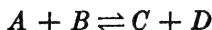
The theory of ionization states that when electrolytes dissolve in water they ionize at once to a greater or less extent into positively charged cations and negatively charged anions. Ionization can be regarded as a reversible chemical reaction between dissolved molecules and their respective ions, and when equilibrium is reached certain of the dissolved molecules are dissociating into ions at a reaction rate which is exactly equal to the rate at which other ions combine to re-form non-ionized molecules. We can indicate such an ionization reaction by means of the general equation:

$$\underset{\text{(non-ionized)}}{MA} \rightleftharpoons M^+ + A^-$$

where MA stands for the dissolved non-ionized molecules of the compound MA, and M^+ the cations and A^- the anions in equilibrium with the non-ionized portion of the dissolved electrolyte. At equilibrium, which is quickly reached when the compound is dissolved, a certain fixed ratio between the non-ionized molecules and the products of their ionization will always be maintained. The ratio between the concentrations of the initial and final products of a reaction is dealt with by the Law of Chemical Equilibrium, and hence in establishing the conditions for equilibrium for the ionization of electrolytes, the law finds here a very important application.

The general equilibrium formula:

$$\frac{C_C \times C_D}{C_A \times C_B} = K$$

which expresses the equilibrium ratio of concentrations in the general reaction:

$$A + B \rightleftharpoons C + D$$

may be transformed for the special reaction of ionization of the electrolyte MA:

$$MA \rightleftharpoons M^+ + A^-$$

into the special form:

$$\frac{C_{M^+} \times C_{A^-}}{C_{MA}} = K.$$

K is an equilibrium ratio and expresses the ratio of the product of the ion concentrations to the concentration of the non-ionized portion of the solute.

Equilibrium Ratios and Ionization Constants.—One can write such an equilibrium ratio and determine its numerical value for any electrolyte, but the ratio will have the same constant value, for all ranges of concentration, *for weakly ionized electrolytes only.* For highly ionized acids and bases and for salts (which, with few exceptions, are highly ionized) the ratio is not constant. For weakly ionized acids, such as $HC_2H_3O_2$, HCN and HNO_2, and for the weakly ionized base, NH_4OH, the ratio is constant for all concentrations. When the ratio is found to be constant for a weak electrolyte, it is known as an ionization constant.

Thus for a weakly ionized monobasic acid HA which ionizes according to the reaction:

$$HA \rightleftharpoons H^+ + A^-$$

the equilibrium is expressed by the relation:

$$\frac{\text{Concentration of } H^+ \text{ ions} \times \text{Concentration of } A^- \text{ anions}}{\text{Concentration of non-ionized molecules}} = K \text{ (Ionization constant)}$$

and the formula becomes

$$\frac{C_{H^+} \times C_{A^-}}{C_{HA}} = K_{(\text{ion})}.$$

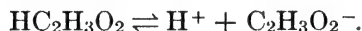
As already stated, an electrolyte is characterized by a true ionization constant only if the equilibrium ratios calculated for a

number of concentrations have the same numerical value, i.e., if the ratios are practically the same for all concentrations. The Law of Chemical Equilibrium can be rigorously applied to ionic equilibria only for weak electrolytes. Whether an electrolyte conforms to the law must be discovered by experiment and calculation.

The ionization constant, for any particular electrolyte of specified concentration, will vary with the temperature, since, as was pointed out on page 16, the extent of ionization varies with the temperature. Changes of pressure have little effect on the ionization constant. The method of calculating ionization constants, the effect of changes in concentration and of added substances and the way ionization equilibria are used in qualitative analysis are illustrated in the following paragraphs for acetic acid, a typical weak electrolyte.

Ionization Equilibrium of $HC_2H_3O_2$

Calculation of the Constant.—Suppose that we take a dilute aqueous solution of acetic acid of such strength that a liter contains one-tenth of a gram-mol (one-tenth of the molecular weight in grams or 6.0032 grams) of dissolved $HC_2H_3O_2$. As a weak electrolyte, it will be ionized to a small extent into H^+ ions and $C_2H_3O_2^-$ ions according to the reaction:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-.$$

The actual degree of ionization at 18° C. is 1.34 per cent (given in Table I, page 14). The respective concentrations in a liter of 0.1 molar acetic acid are therefore 0.1 × 0.0134 or 0.00134 gram-ion of H^+ ions, 0.1 × 0.0134 or 0.00134 gram-ion of $C_2H_3O_2^-$ ions and 0.1 × 0.9866 or 0.09866 gram-mol of non-ionized $HC_2H_3O_2$.

The equilibrium expression for this ionization is written thus:

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{(ion)}.$$

Placing the numerical values for the concentrations of the reacting components in this expression gives the numerical ratio:

$$\frac{(0.1 \times 0.0134) \times (0.1 \times 0.0134)}{(0.1 \times 0.9866)} = 0.0000182.$$

The value 0.0000182 or 1.82×10^{-5}, sometimes, written 0.0_4182 is the ionization constant for $HC_2H_3O_2$. If the equilibrium law holds rigorously for this electrolyte, substantially this same numerical value must be obtained for acetic acid solutions of other concentrations. That this is the fact is shown in the calculation below.

Effect of Dilution.—Suppose that we dilute the above 0.1 molar solution to ten times its volume, thus making a 0.01 molar solution of $HC_2H_3O_2$. One liter of this diluted solution will then contain only one-tenth as much dissolved solute as the first solution considered. If no change in the degree of ionization took place in this more dilute solution, a calculation of the ratio would give a new, different value of $K_{(\text{ion})}$. We know, however, from our study of ionization that the extent of ionization increases with dilution (see page 15) and this means that the equilibrium which became disturbed during dilution is again restored by adjustment of the ratio between ions and non-ionized molecules. The value for the percentage of ionization of a 0.01 molar solution of $HC_2H_3O_2$ at 18° C. is 4.17 per cent (see Table II, page 15). The new concentrations are therefore 0.01×0.0417 or 0.000417 gram-ion of H^+ ions, 0.01×0.0417 or 0.000417 gram-ion of $C_2H_3O_2^-$ ions and 0.01×0.9583 or 0.009583 gram-mol of non-ionized $HC_2H_3O_2$. Inserting these values in the equilibrium expression gives:

$$\frac{(0.01 \times 0.0417) \times (0.01 \times 0.0417)}{(0.01 \times 0.9583)} = 0.0000181.$$

This value for the ionization constant is in close agreement with the value calculated previously for the 0.1 molar solution and shows that the equilibrium law can be rigorously applied to acetic acid solutions. The accepted value is 1.8×10^{-5}.

The method of calculating ionization constants must be mastered by the student, for frequent use will be made of ionic equilibria throughout the experimental work. To calculate the constant for any electrolyte we must know two quantities, namely, the molarity of the solution and the degree of ionization at the specified temperature. It is well for the beginner to resolve each term into its two factors, as shown in the foregoing calculations.

The formula can be simplified by letting α stand for the fraction which is present as ions, $1 - \alpha$ for the non-ionized fraction and M

for the total molar concentration of the dissolved solute. The expression then becomes:

$$M\left(\frac{\alpha^2}{1-\alpha}\right) = K_{(\text{Ion})}.$$

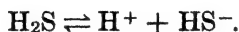
In this form the relationship between dilution and degree of ionization is known as the **Ostwald dilution formula.**

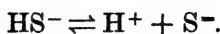
If we know the ionization constant and the molar concentration of a dissolved solute we can calculate the degree of ionization by solving for α in the above equation.

Ionization Equilibria of Other Electrolytes

Acids.—Other acids that follow the equilibrium law more or less closely, that is, those that are rather weakly ionized, are HCN, HNO_2, H_2S, H_2CO_3, $H_2C_2O_4$, H_3AsO_3, H_3AsO_4, H_3PO_4, H_3BO_3. The more strongly ionized acids, such as HCl, HNO_3, H_2SO_4, etc., do not yield the same constant for different concentrations and thus deviate from the law. With the dibasic acids, such as H_2S, H_2CO_3 and $H_2C_2O_4$, which ionize in two stages, there is a primary and a secondary ionization constant.

The equilibrium relationships of H_2S, a weakly ionized dibasic acid, are extremely important. This reagent is used in precipitating many metallic ions as sulfides, and the amount of sulfide ion which this acid yields by its secondary ionization must be carefully regulated. This acid ionizes to a small extent into hydrogen ions and hydrosulfide ions, according to the equation:

$$H_2S \rightleftharpoons H^+ + HS^-.$$

An extremely small number of hydrosulfide ions undergo ionization to yield sulfide, $S^{=}$, ions and an additional minute concentration of hydrogen ions, the secondary stage of ionization being shown by the equation:

$$HS^- \rightleftharpoons H^+ + S^{=}.$$

For the first stage of ionization the equilibrium expression is:

$$\frac{C_{H^+} \times C_{HS^-}}{C_{H_2S}} = K_1 \text{ (Primary ionization constant),}$$

and for the secondary stage it is:

$$\frac{C_{H^+} \times C_{S^=}}{C_{HS^-}} = K_2 \text{ (Secondary ionization constant).}$$

This case of H_2S will be more fully discussed under the applications of the solubility product principle (see page 64).

With tribasic acids, there is a primary, a secondary, and a tertiary ionization constant, corresponding to the three stages of ionization (see Table I, page 14, and Table V, page 51. Thus for H_3PO_4 we have:

$$\frac{C_{H^+} \times C_{H_2PO_4^-}}{C_{H_3PO_4}} = K_1 \text{ (Primary ionization constant)}$$

$$\frac{C_{H^+} \times C_{HPO_4^=}}{C_{H_2PO_4^-}} = K_2 \text{ (Secondary ionization constant)}$$

and

$$\frac{C_{H^+} \times C_{PO_4^\equiv}}{C_{HPO_4^=}} = K_3 \text{ (Tertiary ionization constant).}$$

It has already been pointed out (page 13) that the primary ionization stage takes place to a much greater extent than the secondary, and the secondary more than the tertiary; and accordingly the H^+ ion concentration of acids is due largely to the primary ionization. Primary ionization constants of dibasic and tribasic acids are consequently numerically much larger figures than the secondary and tertiary constants. This will become evident on inspection of Table V. The smaller the degree of ionization, the smaller the constant and the more closely will the electrolyte obey the law of chemical equilibrium.

Bases.—The only commonly used base which can be considered as closely following the law is NH_4OH. The calculation of its ionization constant is not so simple a matter as that for acetic acid, because in a solution of ammonium hydroxide there are, besides a low concentration of NH_4^+ ions and OH^- ions, non-ionized dissolved NH_4OH and dissolved NH_3. The reagent is used extensively, and the equilibrium relationships are very important; the discussion will be taken up later (see page 77).

Salts.—Since salts, as a general rule, are strong electrolytes, no constant values are had for different concentrations. We can, of course, calculate a new value for each particular dilution, but

on the basis of the theory here outlined, we cannot apply it in the same sense that we apply it, for example, to acetic acid and ammonium hydroxide.

TABLE V

IONIZATION CONSTANTS

Electrolyte	Primary	Secondary	Tertiary
HCl	*		
HNO_3	*		
HNO_2	5×10^{-4}		
$HCHO_2$	2×10^{-4}		
$HC_2H_3O_2$	1.8×10^{-5}		
HCN	7×10^{-10}		
H_2SO_4	*	3×10^{-2}	
$H_2C_2O_4$	3.8×10^{-2}	5×10^{-5}	
$H_2C_4H_4O_6$	9.7×10^{-4}	9×10^{-5}	
H_2SO_3	1.7×10^{-2}	1×10^{-7}	
H_2CO_3	3×10^{-7}	6×10^{-11}	
H_2S †	9×10^{-8}	1.2×10^{-15}	
H_3AsO_4	5×10^{-3}	4×10^{-5}	6×10^{-10}
H_3PO_4	1×10^{-2}	2×10^{-7}	4×10^{-13}
H_3AsO_3	6×10^{-10}		
H_3PO_3	6×10^{-10}		
HOH ‡	2×10^{-16}		
$NaOH$	*		
NH_4OH	1.75×10^{-5}		
$Ca(OH)_2$	3×10^{-2}		

* Ionization too great to yield an ionization constant.

† $\frac{(C_{H^+})^2 \times C_{S^-}}{C_{H_2S}} = 1.1 \times 10^{-22}$; $(C_{H^+})^2 \times C_{S^-} = 1.1 \times 10^{-23}$.

‡ $(C_{H^+}) \times C_{OH^-} = 1.2 \times 10^{-14}$.

COMMON-ION EFFECT

In the ionization equilibrium formula it should be noted that the numerator of the ratio is the *product* of the gram-ion concentrations of the ions involved. In the particular cases calculated above for $HC_2H_3O_2$ the concentration of the cation, H^+, is equal to the

concentration of the anion, $C_2H_3O_2^-$, merely because these values were obtained by measuring the ionization of pure solutions of $HC_2H_3O_2$. That the concentrations of each set of ions need not necessarily be equal for equilibrium to be established has a very important application to actual analysis. The concentration of one set of ions may greatly exceed that of the other set of ions and cases actually arise where it becomes desirable or necessary to add another compound containing ions of the same kind as the one or the other set already present. By this means the concentration of one ion can be adjusted to any desired value by varying the concentration of the other ion. The effect on the equilibrum of these added common ions is known as the **common-ion effect** It is illustrated here for $HC_2H_3O_2$.

Suppose that we are carrying out an analytical procedure in an acidic solution and find it desirable to have a low concentration of hydrogen ions present. A weak acid such as $HC_2H_3O_2$ yields, we have seen, a low concentration of H^+ ions, but a still lower concentration can be secured by adding a highly ionized salt of acetic acid such as $NH_4C_2H_3O_2$ or $NaC_2H_3O_2$ to the solution of acetic acid. The effect of the large addition of acetate ions to those already present is greatly to decrease the concentration of the hydrogen ions. That this must be the result can be seen from an actual calculation.

Suppose that, to a liter of 0.1 molar $HC_2H_3O_2$ which ionizes to the extent of 1.34 per cent, we add 0.1 of a gram-mol of $NaC_2H_3O_2$, which in a liter of solution at 18° C. ionizes about 80 per cent. We have at the start 0.00134 gram-ion of $C_2H_3O_2^-$ from the acetic acid and 0.080 gram-ion of the same ion from the added sodium acetate or a total of 0.08134 gram-ion of $C_2H_3O_2^-$. There are also present at the start 0.00134 gram-ion of hydrogen and 0.09866 gram-mol of non-ionized acetic acid. These quantities cannot exist together in these proportions without disturbing the equilibrium, since the ionization constant, 0.0000182, must be satisfied. The only way in which equilibrium can be restored is for acetate ions to combine with an equal number of hydrogen ions and form non-ionized acetic acid until the ratio again satisfies the equilibrium constant. The extent to which the hydrogen-ion concentration is thus lowered and the extent to which the ionization of the acid is repressed are shown by the following calculation. Let x equal the amount by which the H^+ ion and $C_2H_3O_2^-$ ion

concentrations are decreased and the $HC_2H_3O_2$ concentration increased. Substituting in the equilibrium expression:

$$\frac{(0.00134 - x) \times (0.08134 - x)}{(0.09866 + x)} = 0.0000182$$

gives, for x, a value of 0.00129, the amount by which the hydrogen- and acetate-ion concentrations are decreased and the concentration of non-ionized acetic acid is increased. The new hydrogen-ion concentration is therefore $0.00134 - 0.00129 = 0.00005$, showing a greatly decreased acidity.

By making certain approximations we can avoid the above quadratic equation. Let y stand for the final hydrogen-ion concentration. Assume that the final acetate-ion concentration is that of the added $NaC_2H_3O_2$ and that the final concentration of non-ionized $HC_2H_3O_2$ is the same as in pure acetic acid. These assumptions are warranted since it can be seen from the above that the difference from the exact amounts (x above) is practically negligible. We have then:

$$\frac{y \times (0.1 \times 0.80)}{0.1(1 - 0.0134)} = 0.0000182$$

and solving this equation we have:

$$y = 0.0000224$$

which is the new H^+ ion concentration.

Just as an increase of acetate ions will lower the concentration of hydrogen ions which can exist in equilibrium with acetic acid, an increase in hydrogen ions from a strong acid will lower the acetate-ion concentration and repress the ionization of the acetic acid. And further, if a strongly ionized acid, such as HCl, is added to a solution of an acetate, the hydrogen ions together with acetate ions will be used up in forming non-ionized acetic acid. Usually a strongly ionized acid will displace a weaker acid from its salts owing to the repression of the ionization of the less ionized acid.

Buffer Solutions.—By means of common-ion effect it is thus possible to lower and keep in control the concentration of certain ions. If the hydrogen-ion concentration, i.e., the acidity, of a

solution is to be controlled, a weakly ionized acid, such as acetic or formic, is employed together with a salt of the acid, as for example sodium acetate or sodium formate. If the basicity, i.e., the OH^- ion concentration, is to be controlled, NH_4OH and NH_4Cl are used. A reagent thus prepared by mixing a weakly ionized acid or base with a salt of the acid or base, for the purpose of keeping within narrow limits the acidity or basicity of a solution, is known as a buffer solution. The solution is said to be "buffered." Common-ion effect on the equilibrium of the weak electrolyte is the basis of buffer action. Important examples of buffer action are found in analytical procedures, and applications to the qualitative scheme are discussed below.

Applications to the Analytical Procedures.—The most general application that can be made of the behavior of weak electrolytes to the reactions involved in the methods of analysis is that, when mixtures are produced which contain the constituent ions, these ions will combine, because the ionization constant of the weak electrolyte must be satisfied. For example, if a solution undergoing analysis contains an acetate, and a strong acid such as HCl is added, a large amount of the acetate ions will combine with the hydrogen ions from the HCl, to form weakly ionized $HC_2H_3O_2$. This not only lowers the acidity of the solution but may make the regulation of the acidity difficult and uncertain. In general, acidifying a solution containing ions of weak acids will result in the formation of these weak acids. This principle is applied frequently, especially in the analysis of anion Group I, where the weak acids H_2S, H_2CO_3, H_2SO_3, $H_2S_2O_3$, HCN and HNO_2 are formed.

The general principle likewise applies to the presence of ammonium salts when the solution is made basic. The hydroxyl-ion concentration is lowered and the weakly ionized NH_4OH is formed. This behavior is utilized in the test for the NH_4^+ ion.

A solution of $HC_2H_3O_2$ buffered with $NaC_2H_3O_2$ has already been discussed. Two other important examples arise: (1) the regulation of the sulfide ion concentration during the precipitation of sulfide, and (2) the regulation of the OH^- ion concentration in cation Groups III–IV. Both, however, involve also precipitation principles, and for this reason the discussion will be deferred until the solubility product principle is taken up.

THE EQUILIBRIUM LAW APPLIED TO PRECIPITATION: THE SOLUBILITY PRODUCT PRINCIPLE

The equilibrium conditions existing in solutions in which precipitates are formed are extremely important inasmuch as most of the separations and tests of qualitative analysis involve either the formation or the dissolving of precipitates. It is therefore very essential to know, on the one hand, the conditions which lead to the formation of a precipitate and on the other hand what changes take place when a precipitate dissolves. This application of the equilibrium law is known as the **Solubility Product Principle.** In the following paragraphs we will first derive the relationship, then show how the special equilibrium constants, which characterize the equilibrium in such solutions, are calculated and finally apply the principle to the formation and dissolving of precipitates.

Formulation of the Solubility Product Equation.—The solubility product principle states that, in a saturated solution of a difficultly soluble salt, the product of the gram-ion concentrations has a definite numerical value. In the case of the salt AB, whose ions are A^+ and B^-, the relationship, when equilibrium is reached, is expressed by the equation:

$$C_{A^+} \times C_{B^-} = K_{s.p.}$$

where $K_{s.p.}$ is a constant called the solubility product constant and is characteristic of the salt AB.

This relationship can be deduced in the following manner using AgCl as a typical example and following the derivation proposed by Butler (*Chemistry and Industry*, **43**, 634 [1924], and *Jour. Phys. Chem.*, **28**, 438 [1924]). In a saturated solution of silver chloride containing an excess of the solid phase an equilibrium exists between the rate at which the solid dissolves and that at which solid forms. The solid surface may be considered as a lattice of which a portion, x, contains exposed silver ions, the remaining surface $(1 - x)$ having chloride ions exposed. Considering the reversible action to take place separately for Ag^+ ions and for Cl^- ions, the rate at which Ag^+ ions leave the surface may be expressed by k_1x, in which k_1 is a proportionality factor (a velocity constant), and the rate at which Ag^+ ions are deposited on the surface by the

expression $k_2(1 - x)C_{Ag^+}$, since the frequency of deposition will depend upon the concentration, C_{Ag^+}, of the Ag^+ ions in solution, as well as upon the area $(1 - x)$ having exposed chloride ions. At equilibrium the rates of detachment and of attachment of Ag^+ ions are equal and

$$k_1x = k_2(1 - x)C_{Ag^+}. \tag{1}$$

Likewise, the passing of Cl^- ions into solution may be expressed by $k_3(1 - x)$, and the deposition of Cl^- ions on the surface by $k_4xC_{Cl^-}$; accordingly, at equilibrium

$$k_3(1 - x) = k_4xC_{Cl^-}. \tag{2}$$

From equation (1) the concentration of silver ion in solution is

$$C_{Ag^+} = \frac{k_1x}{k_2(1 - x)};$$

and from (2)

$$C_{Cl^-} = \frac{k_3(1 - x)}{k_4x}.$$

For the combined action, we then have:

$$C_{Ag^+} \times C_{Cl^-} = \frac{k_1k_3}{k_2k_4} = K_{s.p.}$$

or

$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.}$$

It should be observed that no numerical or other factor appears for the amount of solid which may be present, an obvious result, since, however much solid may be present, it will have no influence on the concentration of ions in a saturated solution.

This new constant, $K_{s.p.}$, is called the solubility product constant. It is a special equilibrium constant, relating to the equilibrium of the ions in a saturated solution. It can be applied rigorously only for solutions formed from difficultly soluble compounds. The expression means that, in a solution containing ions which by their union produce a difficultly soluble compound, the ions will be in equilibrium when the product of their gram-ion concentrations attains a certain definite, small value, called the solubility product constant. When this constant is reached the solution is saturated with respect to the ions which form the solid. The constant has a different numerical value for each compound

and varies with the temperature for the same compound. It does not strictly apply to solutions containing ions derived from other salts, but holds good, over a limited range, only for solutions of a pure salt.

If the value for the constant is exceeded, the excess ions will separate out as a solid compound (a precipitate). In any solution in which there is undissolved solid, no matter how little or how much, the liquid surrounding the solid will always contain enough of the ions to make the product of their gram-ion concentrations equal to the constant characteristic for that particular solid. This ion relationship as already noted holds only for relatively insoluble compounds.

Calculation of Solubility Product Constants.—Solubility product constants have been determined for practically all the compounds which are obtained as precipitates in analytical work. They can be calculated from the solubility data. The solubility in grams per liter, determined by experiment, is converted into the molar solubility by dividing by the molecular weight of the dissolved compound. From this the concentration of each set of ions may be calculated. If it is known that the ionization of the dissolved solute is not complete, the molar solubility is multiplied by the percentage to which the solution ionizes. For example, the solubility of AgCl at room temperature is 0.0015 gram per liter. Dividing this by the molecular weight of AgCl, 143.34, gives 0.0000106 gram-mol, which is the molar concentration of the dissolved AgCl. This is an extremely dilute solution and may be assumed to be completely ionized. This liter of solution therefore contains 0.0000106 or 1.06×10^{-5} gram-ion of Ag^+ ion and the same concentration of Cl^- ion.

The solubility product equation is:

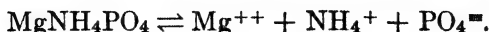
$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.}$$

and substituting numerical values for the concentrations we have:

$$(1.06 \times 10^{-5}) \times (1.06 \times 10^{-5}) = 1.1 \times 10^{-10}$$

giving 1.1×10^{-10} as the $K_{s.p.}$ of AgCl.

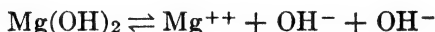
Where three different sets of ions are formed from a dissolved solid, the product of the gram-ion concentration of all three sets is the desired $K_{s.p.}$ In the case of $MgNH_4PO_4$, the precipitate involved in the tests for magnesium and phosphate ions, the

solubility is 0.0086 gram per liter or a molar solubility of 6.3×10^{-5} The ionization of this compound takes place according to the reaction:

$$MgNH_4PO_4 \rightleftharpoons Mg^{++} + NH_4^{+} + PO_4^{\equiv}.$$

The gram-ion concentrations, therefore, in a liter of saturated solution, assuming complete ionization, are 6.3×10^{-5} for each set of ions. The $K_{s.p.}$ is then:

$$\begin{array}{ccccccc} C_{Mg^{++}} & \times & C_{NH_4^{+}} & \times & C_{PO_4^{\equiv}} & = & K_{s.p.(MgNH_4PO_4)} \\ (6.3 \times 10^{-5}) & \times & (6.3 \times 10^{-5}) & \times & (6.3 \times 10^{-5}) & = & 2.5 \times 10^{-13} \end{array}$$

If the dissolved solid, upon ionizing, yields three ions, two of which are alike, the total gram-ion concentration of each set of ions must be determined from the molar solubility of the dissolved solute, after which the total concentration is squared for that set which enters twice in the reaction. This may be made clear in the case of $Mg(OH)_2$. This substance ionizes according to the reaction:

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + OH^{-} + OH^{-}$$

yielding one Mg^{++} ion and two OH^{-} ions for each molecule ionized. The equilibrium expression is therefore:

$$C_{Mg^{++}} \times C_{OH^{-}} \times C_{OH^{-}} = K_{s.p.}$$

or

$$C_{Mg^{++}} \times (C_{OH^{-}})^2 = K_{s.p.}.$$

The molar solubility of $Mg(OH)_2$ at room temperature is 0.000206; hence the concentration of Mg^{++} is 0.000206 gram-ion, and the concentration of the hydroxyl ion is twice as great or 0.000412 gram-ion. The value of the constant is therefore:

$$\begin{array}{ccccc} C_{Mg^{++}} & \times & (C_{OH^{-}})^2 & = & K_{s.p.[Mg(OH)_2]} \\ (0.000206) & \times & (0.000412)^2 & = & 3.5 \times 10^{-11} \end{array}$$

Confusion in calculations involving solubility product relationships will be avoided if it is always remembered (1) to use the *total* concentration of each set of ions and (2) to square or cube this total concentration according to whether the particular set is involved two or three times in the reaction. In general, to

calculate solubility product constants from given solubility data, compute the total ion concentration of each set of ions involved, raising similar sets to powers corresponding to the number of times these sets are involved in the equilibrium and then taking the product of these powers as the desired $K_{s.p.}$

Solubility product constants of a number of precipitates are given in Table VI, the data having been collected from various sources. Constants for sulfides are given in a separate table. (See page 66.)

The values for certain of these compounds have been obtained by methods other than by calculation from solubility data, and in some cases the actual degree of ionization has been taken into account; for these reasons in these cases the numerical value is not in exact agreement with results obtained by calculations based solely on solubility data.

TABLE VI

SOLUBILITY PRODUCT CONSTANTS

Compound	$K_{s.p.}$	Compound	$K_{s.p.}$
$AgCl$	1.1×10^{-10}	$MgNH_4PO_4$	2.5×10^{-13}
$AgBr$	3.5×10^{-13}	$MgCO_3$	2.6×10^{-5}
AgI	1.7×10^{-16}	$CaCO_3$	1.7×10^{-8}
Hg_2Cl_2	2.0×10^{-18}	$SrCO_3$	4.6×10^{-9}
$PbCl_2$	2.4×10^{-4}	$BaCO_3$	1.8×10^{-9}
$PbCrO_4$	1.7×10^{-14}	$BaCrO_4$	2.3×10^{-10}
$PbSO_4$	2.3×10^{-8}	SrC_2O_4	1.4×10^{-7}
$Fe(OH)_3$	1.1×10^{-36}	CaC_2O_4	3.9×10^{-9}
$Fe(OH)_2$	1.6×10^{-14}	$SrSO_4$	3.6×10^{-7}
$Mn(OH)_2$	4.0×10^{-14}	$BaSO_4$	1.2×10^{-10}
$Zn(OH)_2$	1.0×10^{-18}	$CaSO_4$	2.2×10^{-4}
$Mg(OH)_2$	3.5×10^{-11}		

Application of the Solubility Product Principle to Precipitation.—The solubility product constant gives a measure of the concentration of ions which are in equilibrium in a saturated solution of a sparingly soluble compound. This value must be reached to establish equilibrium and must be exceeded before a solid, i.e. a precipitate, will separate out. Since the constant is a *product* of two or more factors expressing concentration of ions in equilibrium, these concentrations need not necessarily be equivalent

to each other as was the case in calculating the constants from pure solutions of the compound; all that is required for equilibrium to be established is for the *product* of the gram-ion concentrations to reach the numerical value of the constant for the compound in question. What happens then during the formation of a precipitate is this: Precipitating ions are added in the form of a solution of an electrolyte to the solution which contains the ions to be precipitated. When an amount of precipitating ions is added such that the product of the ion concentrations (the gram-ion concentration of precipitating ions $\times$ gram-ion concentration of ions to be precipitated) is exactly equal to the $K_{s.p.}$, the ions will be in equilibrium and the solution saturated. Addition of a further amount of precipitating reagent will result in the formation of a precipitate, since the solution is already saturated with ions. The solid will continue to separate during the addition of precipitating ions until the ions whose precipitation is desired have been practically, but not entirely, removed from solution. At all times after a precipitate has initially formed, the solution surrounding it contains the two or more sets of ions in such amounts that the product of their gram-ion concentrations always equals the solubility product constant.

Before considering further the extent to which it is possible to remove ions by precipitation, let us apply the principle to the formation of a precipitate of AgCl. Suppose it is desired to make a qualitative test for silver in a solution of $AgNO_3$ which is 0.0001 molar. At this dilution the solution is practically completely ionized so that the gram-ion concentration of silver ion is 0.0001. The quantity of chloride ion required before a precipitate of AgCl will form can be readily calculated from the $K_{s.p.}$ expression:

$$C_{Ag^+} \times C_{Cl^-} = K_{(s.p.\ of\ AgCl)}$$

$$0.0001 \times x = 1.1 \times 10^{-10}$$

from which $x = 0.000001$ gram-ion of Cl^- ion, the amount which must be added in the form of HCl, NaCl or some other soluble chloride to saturate the solution. An amount beyond this will give a precipitate of AgCl, i.e., the desired test for silver. As more and more chloride ions are added they will at once unite with silver ions, precipitating increasing quantities of AgCl and progressively

lowering the concentration of silver ions remaining in solution. It should be remarked that when an excessively large amount of precipitating agent is added, in the case of AgCl and certain other salts, the precipitate begins to redissolve.

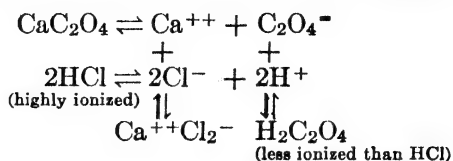
Common-Ion Effect Involved in Precipitation.—As long as AgCl continues to form, silver ions and chloride ions are being removed in equal quantities, and to satisfy the equilibrium requirements the supply of ions must be maintained by adding more chloride ions. A point is eventually reached when the concentration of chloride ions is greatly in excess of silver ions but still equilibrium is maintained. What is required therefore to cause the reaction to run practically to completion and to insure practically complete precipitation (and separation) is to add an excess of precipitating ions. An excess of precipitating agent will have the effect of forcing more of the solid to separate out, analogous to the effect of a large excess of common ions in repressing the ionization of weak electrolytes. The effect on the equilibrium in both cases is to lower the concentration of the other set of ions.

In following the course of ionic changes during precipitation we must recognize two stages, namely, first, the stage at which equilibrium is first established when the $K_{s.p.}$ is reached and beyond which precipitation will take place; and, second, the final stage in which the concentration of precipitating ion is greatly in excess of that for the ions whose (practical) complete removal is desired. At all times after the first stage, the product of the concentrations is numerically equal to the $K_{s.p.}$ of the compound being precipitated. Absolutely complete removal of ions is, according to this principle, impossible, but for practical purposes of separation the precipitation is sufficiently complete.

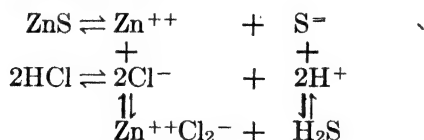
Application of the Solubility Product Principle to the Dissolving of Precipitates.—Inasmuch as the solution surrounding any precipitate is saturated with respect to the ions which form that precipitate, the ions are in equilibrium with each other. If the concentration of the one or of the other or of both ions is lowered the equilibrium will be disturbed and more solid will dissolve in order to restore equilibrium. Thus, increasing the amount of solvent will lower the concentration of both ions and more solid dissolves at the greater dilution. Or the addition of a reagent which will cause a change in the degree of ionization, or will liberate a gas or form a complex ion, will disturb the equilibrium and

remove ions from solution. For example, calcium oxalate will dissolve in dilute HCl. This is explained as follows:

When HCl is added to CaC_2O_4 the equilibria shown below are set up:

$$\begin{array}{lcccc} & CaC_2O_4 \rightleftharpoons & Ca^{++} & + & C_2O_4^{=} \\ & & + & & + \\ & 2HCl \rightleftharpoons & 2Cl^- & + & 2H^+ \\ & \text{(highly ionized)} & \updownarrow & & \updownarrow \\ & & Ca^{++}Cl_2^- & & H_2C_2O_4 \\ & & & & \text{(less ionized than HCl)} \end{array}$$

The $C_2O_4^{=}$ ions in equilibrium with Ca^{++} ions are used up in forming oxalic acid, thus disturbing the equilibrium, and in order to restore it more solid CaC_2O_4 must dissolve and ionize. The H^+ ion concentration from the HCl is lowered correspondingly, owing to the formation of a less ionized acid. Final equilibrium will be established when all the solid CaC_2O_4 has dissolved.

As an example of the formation of a gas, the dissolving of ZnS in HCl may be cited. The ionic changes and the equilibria finally established may be diagrammed thus:

$$\begin{array}{lcccc} ZnS \rightleftharpoons & Zn^{++} & + & S^{=} \\ & + & & + \\ 2HCl \rightleftharpoons & 2Cl^- & + & 2H^+ \\ & \updownarrow & & \updownarrow \\ & Zn^{++}Cl_2^- & + & H_2S \end{array}$$

One of the products of this reaction, H_2S, is a gas which, being slightly soluble, escapes from the solution, thus lowering the sulfide-ion concentration; to maintain the equilibrium between sulfide ions and zinc ions, demanded by the $K_{s.p.}$, more solid ZnS must dissolve. Final equilibrium will be attained only when all the ZnS has dissolved.

The formation of complex ions as a means of disturbing equilibrium will be discussed in a later section.

Reactions of precipitation run practically to completion because a comparatively small concentration is required for equilibrium, the $K_{s.p.}$ values being small numbers. Many reactions taking place during the dissolving of solids are due to free ions being removed through the action of the solvent.

Fractional Precipitation

The foregoing discussion of the theory of precipitation has considered the simple case of a single precipitate being formed.

The situation is more complicated where two or more sets of ions are present in the same solution, both sets capable of being precipitated by the same reagent. This relationship is termed **fractional precipitation.** The questions arise, which set will be precipitated first, and will the first set be completely precipitated before the second set begins to react with the precipitant?

Obviously, when a precipitating ion is added to a solution which contains two kinds of ions both of which can form insoluble salts, the solution will become saturated with respect to the more insoluble salt before it likewise becomes saturated with respect to the more soluble salt. For example, a solution containing equal concentrations of Br^- ions and Cl^- ions will become saturated, when Ag^+ ions are added, with respect to Ag^+ and Br^- before the saturation value for Ag^+ and Cl^- is reached because the $K_{s.p.}$ of AgBr is smaller than that of AgCl. Consequently AgBr will begin to precipitate first. Upon the continued addition of Ag^+ the $K_{s.p.}$ of AgCl will eventually be reached, when both AgBr and AgCl are being precipitated simultaneously. The concentrations of Br^- and Cl^- then bear a constant ratio to each other. This ratio is equal to the ratio of the respective solubility product constants:

$$\frac{K_{s.p.(AgBr)}}{K_{s.p.(AgCl)}} = \frac{3.5 \times 10^{-13}}{1.1 \times 10^{-10}} = \frac{C_{Br^-}}{C_{Cl^-}} = 3.2 \times 10^{-3}.$$

This means that, as simultaneous precipitation of both salts takes place, the concentration of Br^- ions in solution is approximately one thousand times less than that of the Cl^- ions.

Applications of the Solubility Product Principle to the Procedures of Analysis.—As this principle is involved every time a precipitate is formed or one is caused to dissolve, a few specific examples will here be discussed. The simplest involve the precipitation of single salts; a more complicated one will consider the simultaneous precipitation of two similar salts, and finally two important applications where common-ion effect becomes important will be discussed.

In respect to the precipitation of AgCl by the addition of HCl to a small quantity of the Ag-test solution, a simple calculation will show how much precipitating reagent is necessary to establish equilibrium. The Ag-test solution contains 1 mg. (0.001 gram) of Ag^+ ion in 1 cc.; in a liter of this solution there is

1000×0.001 or 1 gram of Ag^+ ion. The gram-ion concentration is therefore $1 \div 107.88$ (the atomic weight of Ag) or approximately 1×10^{-2}. If x represents the chloride-ion concentration required for equilibrium, from the solubility product equation we have:

$$C_{Ag^+} \times C_{Cl^-} = K_{s.p.(AgCl)}$$
$$1 \times 10^{-2} \times x = 1.1 \times 10^{-10}.$$

From this, x is approximately 1×10^{-8}, the chloride-ion concentration required for saturation, any quantity beyond this resulting in the precipitation of AgCl. The gram-ion quantity required for precipitation in 1 cc. or 1 drop can now readily be found.

In much the same manner, the chloride-ion concentration required to start precipitation of Hg_2Cl_2 in a test solution containing 1 mg. of Hg_2^{++} per cc. can be calculated. The mercurous-ion concentration (quantity in 1 liter) is 1 gram $\div 2 \times 200.61 = 2.4 \times 10^{-3}$. From the solubility product equation:

$$C_{Hg_2^{++}} \times (C_{Cl^-})^2 = K_{s.p.(Hg_2^{++}Cl_2^-)}$$
$$(2.4 \times 10^{-3}) \times (x)^2 = 2.0 \times 10^{-18}$$

the value of x is approximately $1 \times 10^{-7.5}$.

Instances where two or more similar precipitates are formed by the addition of the same reagents are the group precipitations. Thus, in the cation analysis, Groups I, II, III and IV are precipitated, respectively, as chlorides, sulfides, hydroxides and sulfides, and carbonates and in the anion analysis, the calcium, barium and silver salts are formed, and where several members of the group are present, the order of initial formation of individual solid depends upon the magnitude of the solubility product constant as well as upon the concentration of each ion. Such an example of fractional precipitation has already been discussed for AgCl and AgBr.

Common-ion effect becomes particularly important in the regulation of the sulfide-ion concentration during precipitation of the sulfides of Group II. The theory involved here is discussed below.

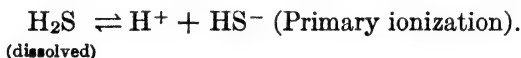
Theory of the Sulfide Precipitation.—If H_2S is passed into neutral solutions containing ions such as Hg^{++}, Cu^{++}, Mn^{++}, Fe^{++}, Zn^{++}, the corresponding sulfides will be formed; some of the sulfides, it is true, will precipitate more rapidly than others,

but eventually all will be precipitated. If the acidity is properly adjusted and H_2S then passed in, only the sulfides of Group II will be precipitated. These facts form the basis for the separation of Group II from Group III.

To explain the action of H_2S as a precipitating agent under these conditions, the following three points must be considered:

1. The ionization of H_2S.
2. The solubility product constants of the sulfides of these two groups.
3. The effect of a common ion on the H_2S equilibrium.

1. *The Ionization of H_2S.*—Hydrogen sulfide is a weakly ionized dibasic acid. It dissolves to some extent in water, forming at room temperatures a solution which is about 0.1 molar. It ionizes in two stages forming first H^+ ions and hydrosulfide, HS^-, ions:

$$\underset{\text{(dissolved)}}{H_2S} \rightleftharpoons H^+ + HS^- \text{ (Primary ionization).}$$

The hydrosulfide ions further ionize to a slight extent into sulfide ions, and hydrogen ions, according to the reaction:

$$HS^- \rightleftharpoons H^+ + S^= \text{ (Secondary ionization).}$$

The primary and secondary ionization constants of H_2S and the concentrations of hydrogen ion, hydrosulfide ion and sulfide ion which can exist in equilibrium with dissolved non-ionized H_2S have been determined by experiment. It has been found that in a liter of saturated solution of H_2S dissolved in water at 25° C. the concentrations are respectively 0.95×10^{-4} gram-ion of hydrogen ion, 0.95×10^{-4} gram-ion of hydrosulfide ion, 1.2×10^{-15} gram-ion of sulfide ions and 0.1 gram-mol of H_2S. If we combine the equilibrium expressions for the primary and secondary ionization of H_2S, namely:

$$\frac{C_{H^+} \times C_{HS^-}}{C_{H_2S}} = K_1 \text{ (Primary)} \quad \text{and} \quad \frac{C_{H^+} \times C_{S^-}}{C_{HS^-}} = K_2 \text{ (Secondary)}$$

we obtain the expression:

$$\frac{(C_{H^+})^2 \times C_{S^=}}{C_{H_2S}} = K_3 \text{ (Ionization constant of } H_2S) = 1.1 \times 10^{-22}.$$

Since, however, we are mainly interested in the amount of

sulfide ion which is available for the precipitation of sulfides, and in the amount of H^+ ion which can be regulated at will, it is more convenient to rewrite the above expression in the form of the product of the ions, by transposing the factor C_{H_2S}, which is practically constant (0.1 gram-mol). The product of the square of the hydrogen-ion concentration and the sulfide-ion concentration becomes:

$$(C_{H^+})^2 \times C_{S^=} = 1.1 \times 10^{-22} \times 0.1 = 1.1 \times 10^{-23}.$$

In a liter of saturated H_2S the value of H^+ is, as already stated, 0.95×10^{-4}, and for $S^=$ it is 1.2×10^{-15}. Inasmuch as the above product represents an equilibrium condition, the value of 1.1×10^{-23} will always be maintained, though the concentration of H^+ or $S^=$ may be varied at will. If the H^+ ion concentration is greatly increased by the addition of a strong acid like HCl, the $S^=$ ions in equilibrium must greatly decrease; or, if the H^+ ions are practically removed by the addition of a base like NH_4OH, the $S^=$ ion concentration becomes enormous.

2. *Solubility Product Constants of Sulfides.*—In order for a precipitate of any sulfide to form, the product of the ion concentration of the cation and that of the sulfide ion must exceed the value of the $K_{s.p.}$ of the sulfide in question. The solubilities in grams and in mols per liter and the solubility product constants for a number of sulfides are given in the table below.

TABLE VII

Sulfide	Solubility in Grams per Liter	Solubility in Mols per Liter	Solubility Product Constant ($K_{s.p.}$)
HgS	1.5×10^{-24}	6.3×10^{-27}	4.0×10^{-53}
CuS	8.8×10^{-21}	9.2×10^{-23}	8.5×10^{-45}
CdS	8.6×10^{-13}	6.0×10^{-15}	3.6×10^{-29}
PbS	4.9×10^{-12}	2.0×10^{-14}	4.2×10^{-28}
ZnS	3.3×10^{-10}	3.5×10^{-12}	1.2×10^{-23}
FeS	3.4×10^{-8}	3.9×10^{-10}	1.5×10^{-19}
MnS	3.3×10^{-6}	3.8×10^{-8}	1.4×10^{-15}

These data have been collected from various sources. Data for the other insoluble sulfides of the metals either have not been determined or else are unreliable. Data for CoS and NiS are frequently included in solubility product tables, but since these sulfides exist in several modifications (page 155) the values are not comparable to those for other sulfides given in the table.

It should be recalled that the constants represent solutions saturated with respect to the metallic and sulfide ions, and that, using such concentrations of metallic ions as employed in the test solutions, a sufficient sulfide-ion concentration from the ionization of H_2S can be maintained to exceed the value for the respective solubility product constants. The extremely small values of the constants for HgS and CuS, for instance, are quickly reached and exceeded; whereas, using test solutions of the same strength for, say, zinc and manganese, relatively much greater concentrations of sulfide ion are required for saturation and subsequent precipitation of ZnS and MnS. It is convenient for the analyst to make a separation of the sulfides into two main groups (Group II and Group III). This is done by regulating the amount of $S^{=}$ ion available for precipitation. The $S^{=}$ ion concentration may be controlled by making use of the common-ion effect, as will be seen below.

3. *The Effect of a Large Concentration of Hydrogen Ions on the H_2S Equilibrium.*—In order to bring about a division of the sulfides into two groups, the amount of $S^{=}$ ion which is in equilibrium with non-ionized H_2S must be decreased to a more or less definite small value, and this in turn is accomplished by increasing the H^+ ion concentration through the addition of HCl. The order in which the sulfides are precipitated by successively decreasing the amount of HCl added (decreasing the amount of common ion) is: As_2S_3, HgS, CuS, Sb_2S_3, Bi_2S_3, SnS_2, CdS, PbS, SnS, ZnS, CoS, NiS, FeS, MnS.

For practical analytical purposes it is best to precipitate the sulfides of arsenic, antimony and tin; mercuric mercury, copper, bismuth, cadmium and lead and treat these as Group II. The cations of zinc, iron, nickel, cobalt, manganese, together with aluminum and chromium, are then left in solution to be later precipitated under conditions of high $S^{=}$ ion concentration and treated as Group III. If sufficient HCl is added so as to make the solution approximately 0.1 molar with respect to hydrogen-ion con-

centration the new $S^{=}$ ion concentration can be calculated as follows:

$$(0.1)^2 \times C_{S^=} = 1.1 \times 10^{-23}.$$

Therefore, $$C_{S^=} = 1.1 \times 10^{-21}.$$

This extremely small concentration of ionic sulfur is still sufficient to cause precipitation of the metallic ions included in Group II.

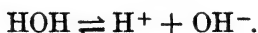
Summarizing, the theory of the sulfide precipitation can be stated thus: By the repression of the sulfide ions through the addition of common H^+ ions the solubility product constants are exceeded only in case of the cations of Group II.

THE EQUILIBRIUM LAW APPLIED TO HYDROLYSIS

Aside from the two general applications of the equilibrium law discussed in the foregoing sections, the one referring to the equilibrium of ions and non-ionized molecules in solutions of weak electrolytes and characterized by ionization constants and the other relating to the equilibrium of ions in saturated solutions of difficultly soluble compounds and designated by solubility product constants, and the special case of complex ion formation, there are several other instances of equilibria now to be considered. One of these involves the ions of water and the reaction of salts with water.

Hydrolysis of Salts

The Water Equilibrium.—Water behaves as a very weak electrolyte, ionizing to an extremely small extent into hydrogen and hydroxyl ions according to the reaction:

$$HOH \rightleftharpoons H^+ + OH^-.$$

At 25° C. the percentage of ionization is but 0.0000002 (see Table I, page 14). The equilibrium ratio:

$$\frac{C_{H^+} \times C_{OH^-}}{C_{HOH}} = K_{(ion)}$$

at this temperature has been found by experiment to be 1×10^{-16}. Since, however, the concentration of non-ionized HOH is enormous compared with the small concentration of the ions, it is customary

and more convenient to combine this factor with the constant of the above ratio and write the equilibrium in the following form:

$$C_{H^+} \times C_{OH^-} = K \times C_{HOH} = K_w.$$

The new constant, K_w, is then the product of the concentrations of hydrogen and hydroxyl ions. At 25° C. the value of K_w, determined directly, is 1.2×10^{-14}; at 100° C. it is 5×10^{-12}, which shows that at higher temperatures water is more highly ionized. In a liter of pure water at 25° C., the concentrations of hydrogen ions and hydroxyl ions are the same, namely, approximately 1×10^{-7} gram-ion of each.

In any aqueous solution, at 25° C., the product of the gram-ion concentrations of hydrogen and hydroxyl always equals 1.2×10^{-14}. If the solution is theoretically neutral the value of H^+ ion and of OH^- ion is about 10^{-7}. Any solution which has a hydrogen-ion concentration greater than 1×10^{-7} is, by definition, acidic; and one having a hydroxyl-ion concentration greater than 1×10^{-7}. is basic. Thus a solution which has a hydrogen-ion concentration of, say, 1×10^{-5} is acidic and must have in equilibrium with it a hydroxyl-ion concentration of 1×10^{-9}, since their product must be approximately 1×10^{-14}. No aqueous solution, no matter whether it is an acid, a base or a salt, can contain at the same time concentrations of H^+ ions and OH^- ions such that their product is greater or less than 1.2×10^{-14}. We can therefore indicate whether a solution is acidic, neutral or basic by designating either its hydrogen-ion or its hydroxyl-ion concentration. It is conventional to use the hydrogen-ion concentration. We may express the concentration in decimal form, in an exponential form or by what is known as the *p*H value.

The Experimental Determination of Hydrogen-Ion Concentration. Colorimetric Method.—There are two experimental methods for the measurement of the hydrogen-ion concentration of solutions —the colorimetric and the potentiometric. The colorimetric method depends upon the fact that certain organic dyestuffs have the property of changing their color over definite narrow ranges of H^+ ion concentration. (These are the substances used as indicators in neutralization titrations in volumetric quantitative analysis.) If, then, we wish to determine the (approximate) H^+ ion concentration of a solution we may add drops of the dyestuffs to portions of the sample and in this way find the range between

which two indicators are sensitive. For example, methyl orange has a yellow color in solutions which have a H^+ ion concentration of $1 \times 10^{-4.4}$ or less, and Congo red has a blue-violet color in solutions of a H^+ ion concentration greater than $1 \times 10^{-5.2}$. Consequently, if the sample is yellow in methyl orange and blue-violet in Congo red, the H^+ ion concentration lies between $1 \times 10^{-4.4}$ and $1 \times 10^{-5.2}$.

The Potentiometric Determination of Hydrogen-Ion Concentration.—This method depends upon measuring the electromotive force produced in an electrolytic cell; one "half-cell" consists of a hydrogen electrode which dips into a solution which is molar with respect to H^+ ions, and the other " half-cell " is made up of a hydrogen electrode dipping into the solution the hydrogen-ion concentration of which is to be determined. The two half-cells are joined by a U-tube filled with a conducting liquid, and the electrodes are joined to a potentiometer. The potential read in volts on the potentiometer is related to the concentrations in the two half-cells by the Nernst equation:

$$E = 0.059 \log \frac{1}{C_{H^+}}$$

in which 0.059 is a constant at 25° C., 1 is the H^+ ion concentration in the molar solution and C_{H^+} is the H^+ ion concentration in the unknown sample. By measuring E, the equation can be solved for C_{H^+}.

***p*H Values.**—In order to obviate a logarithmic calculation, a convention, first proposed by Sörensen, has been adopted, namely to let the symbol *p*H stand for $\log \frac{1}{C_{H^+}}$. According to this, **the *p*H value is the logarithm of the reciprocal of the H^+ ion concentration.** If, in a potentiometric determination, the voltage, E, is measured, the *p*H is directly

$$\frac{E}{0.059} = \log \frac{1}{C_{H^+}} = p\text{H}.$$

The use of the *p*H scale may be illustrated in the following example.

Suppose that the H^+ ion concentration of a certain solution is

0.00001 or 1×10^{-5}. Then, since $pH = \log \frac{1}{C_{H^+}}$, and C_{H^+} is 1×10^{-5},

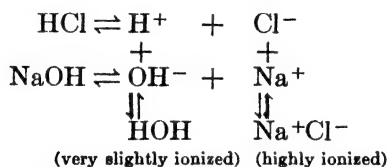
$$\log \frac{1}{1 \times 10^{-5}} = \log 1 - \log (1 \times 10^{-5})$$

$$= 0 - (-5)$$

$$= + 5.$$

The pH value of the solution is therefore 5. Since the C_{H^+} is greater than 10^{-7} the solution is acidic. According to the pH scale, values of pH of less than 7 represent acidic solutions; a value of exactly 7 is a neutral solution, and values beyond this designate basic solutions.

Neutralization of Acids and Bases.—On the basis of the water equilibrium, the mechanism of the neutralization of an acid by a base, or vice versa, becomes more intelligible. Take, for example, the reaction between HCl and NaOH. The ionization steps and final equilibrium can be shown thus:

$$\begin{array}{lccc} HCl \rightleftharpoons & H^+ & + & Cl^- \\ & + & & + \\ NaOH \rightleftharpoons & OH^- & + & Na^+ \\ & \downarrow\uparrow & & \downarrow\uparrow \\ & HOH & & Na^+Cl^- \\ & \text{(very slightly ionized)} & & \text{(highly ionized)} \end{array}$$

The slightly ionized product, HOH, must be in equilibrium with H^+ ions and OH^- ions and the equilibrium equation:

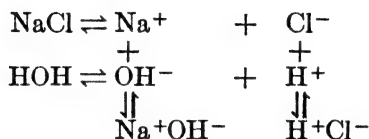
$$C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$$

must be satisfied. In this particular instance, the concentrations of H^+ ion and OH^- ion are practically equal, and of the order of 1×10^{-7}, and the neutralization of the acid by the base will stop when these almost negligible amounts of ions are left in the solution. In other cases, where the salt formed by neutralization is hydrolyzed the final concentrations of H^+ ions and OH^- ions may not be exactly equal but their product must equal 1.2×10^{-14}.

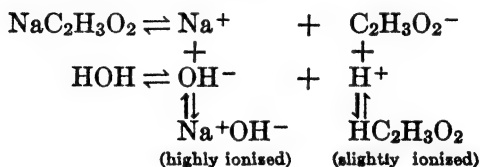
Hydrolysis of Salts.—Since hydrogen and hydroxyl ions are present in all aqueous solutions, these may react with other ions present and form acids or bases. Decomposition of salts by water is termed hydrolysis. It can thus be regarded as the reverse of

neutralization. The question arises, to what extent will hydrolysis take place in solutions of certain salts? The answer depends upon the type of salt constituting the solute. We can distinguish four types of salts.

1. If the salt is one originally formed by the neutralization of a strong acid by a strong base, such as NaCl, the tendency to re-form the original acid, HCl, and the original base, NaOH, will be practically nil. This follows from the fact that the products of the hydrolysis reaction:

$$\begin{array}{lcl} NaCl \rightleftharpoons Na^+ & + & Cl^- \\ \qquad\quad + & & + \\ HOH \rightleftharpoons OH^- & + & H^+ \\ \qquad\quad \downarrow\uparrow & & \downarrow\uparrow \\ \qquad\quad Na^+OH^- & & H^+Cl^- \end{array}$$

a strongly ionized base, NaOH, and an equally strongly ionized acid, HCl, will have practically no effect in changing the hydrogen- or hydroxyl-ion concentration in equilibrium with HOH. The solution will be neutral, since the H^+ ion and OH^- ion concentrations remain the same, about 1×10^{-7}. Hydrolysis does not take place to any appreciable extent in salt solutions of this type.

2. The salt of a strong base and a weak acid, such as $NaC_2H_3O_2$, will, however, show a tendency to react with the ions of water. This can be shown by the reactions:

$$\begin{array}{lcl} NaC_2H_3O_2 \rightleftharpoons Na^+ & + & C_2H_3O_2^- \\ \qquad\qquad\quad + & & + \\ \qquad HOH \rightleftharpoons OH^- & + & H^+ \\ \qquad\qquad\quad \uparrow\downarrow & & \downarrow\uparrow \\ \qquad\qquad\quad Na^+OH^- & & HC_2H_3O_2 \\ \qquad\quad \text{(highly ionized)} & & \text{(slightly ionized)} \end{array}$$

The slightly ionized acetic acid uses up H^+ ions thus disturbing the water equilibrium, causing more water to ionize and eventually, when equilibrium is reached, having in solution a greater concentration of OH^- ions than of H^+ ions. The other product of the hydrolysis, NaOH, is highly ionized and results therefore in the accumulation of an excess of hydroxyl ions. Solutions of salts of this type will show an alkaline test toward litmus paper, and this fact is utilized (see page 218) in obtaining indications of the presence of anions (acid radicals) such as acetates, sulfides, car-

bonates, borates and cyanides, present in the mixture as salts of this type.

The extent to which hydrolysis will take place, and the hydroxyl-ion concentration as well as the *p*H value, in solutions of salts of this type can readily be calculated from the equilibrium relationships. The ionization constant for $HC_2H_3O_2$, as already shown (page 47), is expressed by the ratio:

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{(\text{ion})} = 1.8 \times 10^{-5} \quad (1)$$

and this must be satisfied when equilibrium is established. The water equilibrium:

$$C_{H^+} \times C_{OH^-} = K_w = 1.2 \times 10^{-14} \quad (2)$$

must also be satisfied.

Combining the two equilibrium expressions by dividing (2) by (1) gives the hydrolysis constant:

$$\frac{C_{HC_2H_3O_2} \times C_{OH^-}}{C_{C_2H_3O_2^-}} = \frac{K_w}{K_{(\text{ion})}} = K_{(\text{hydrolysis})}$$

The value of the hydrolysis constant for this salt is therefore:

$$\frac{K_w}{K_{(\text{ion})}} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}} = 6.7 \times 10^{-10}.$$

Inasmuch as, through the formation of $HC_2H_3O_2$, the hydrogen-ion concentration is decreased, resulting in a corresponding increase in hydroxyl-ion concentration, the final OH^- ion concentration will be equal to the concentration of non-ionized $HC_2H_3O_2$, and the final concentration of $C_2H_3O_2^-$ ion will be less than that in the original solution before hydrolysis has taken place. The final hydroxyl-ion concentration, as well as the amount of acetic acid formed, can readily be determined by the equilibrium equation. Thus, for a 0.1 molar solution of $NaC_2H_3O_2$, assuming complete ionization of the dissolved salt, we have, letting x equal C_{OH^-} as well as $C_{HC_2H_3O_2}$:

$$\frac{C_{OH^-} \times C_{HC_2H_3O_2}}{C_{C_2H_3O_2^-}} = \frac{x \times x}{0.1 - x} = 6.7 \times 10^{-10}.$$

Since the concentration of anion is only slightly lowered from

that originally present, we may drop x from the factor $(0.1 - x)$ and have therefore:

$$\frac{x^2}{0.1} = 6.7 \times 10^{-10}$$

from which $x = 8.2 \times 10^{-6}$. The OH^- ion concentration is 8.2×10^{-6} or approximately 1×10^{-5}. The hydrogen-ion concentration of this solution is then approximately 1×10^{-9}, and the pH value 9. The concentration of $HC_2H_3O_2$ formed is likewise approximately 1×10^{-5}, while the degree of hydrolysis is approximately $(1 \times 10^{-5} \div 0.1) \times 100$ or 0.01 per cent.

3. Salts of weak bases and strong acids are also hydrolyzed to a greater or less extent, owing, in this case, to the formation of a slightly ionized (or insoluble) base. The formation of the base removes free hydroxyl ions from the solution and results in the accumulation of an excess of hydrogen ions from the highly ionized, strong acid. Such solutions react acidic toward litmus. The chlorides of ammonium, iron and aluminum are examples of salts of this type. The student should write the ionization and hydrolysis reactions of salts of this type to satisfy himself of the truth of the above statements. The hydrolysis constant can be deduced from the equilibrium relationships in exactly the same way as was done above and will lead to the following expression:

$$\frac{C_{H^+} \times C_{(\text{non-ionized base})}}{C_{(\text{cation})}} = \frac{K_{(w)}}{K_{(\text{ion for base})}} = K_{(\text{hydrolysis})}.$$

By a calculation from the data, similar to the method illustrated for $NaC_2H_3O_2$, the extent of the hydrolysis can be determined and the concentrations of H^+ ion and OH^- ion found.

Many examples of hydrolysis of this type will be encountered in the experimental part of this book.

4. Finally, the solutions of salts formed by neutralization of weak acids by weak bases are extensively hydrolyzed. This follows from the fact that on the one hand the weakly ionized acid produced by hydrolysis uses up H^+ ions as fast as they are formed from the ionization of the water, until the ionization constant of the weak acid is satisfied. On the other hand, the weakly ionized base, formed simultaneously, consumes the OH^- ions from the water, until the ionization constant for the weak base is satisfied. The hydrolysis will stop when the constants for both acid and base

are reached, and if both are approximately of the same magnitude, the residual H^+ ion and OH^- ion concentrations will be about the same and of the order of 1×10^{-7}.

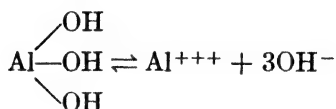
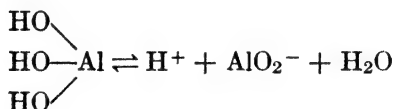
AMPHOTERISM

An amphoteric compound is one which has the properties both of an acid and of a base. Many hydroxides are amphoteric and ionize as acids and as bases. This is especially true of the hydroxides of the elements occupying positions near the middle of the Periodic Table (see page 250). Of special interest to us are the hydroxides of aluminum, chromium, zinc, antimony and tin.

Aluminum hydroxide will be taken here as a typical example to illustrate the behavior of amphoteric hydroxides. The ionization of $Al(OH)_3$ as a base can be represented thus:

$$Al(OH)_3 \rightleftharpoons Al^{+++} + 3OH^-$$

and as an acid:

$$(HO)_3Al \rightleftharpoons H^+ + AlO_2^- + H_2O$$

yielding H^+ ion from its primary ionization, the meta-aluminate ion, AlO_2^-, and H_2O. In an aqueous solution of aluminum hydroxide (a very dilute one, since $Al(OH)_3$ is very sparingly soluble in water) there exist aluminum and hydroxyl ions in equilibrium with hydrogen and meta-aluminate ions. On the basis of this double equilibrium we can see, on the one hand, why $Al(OH)_3$ will dissolve in acids to form aluminum salts, and, on the other hand, why it will dissolve in bases to form aluminates. In the first case, the hydroxyl ions coming from the ionization of $Al(OH)_3$ are used up by the hydrogen ions from the acid and this results in more of the solid being dissolved to restore equilibrium; the comparatively high hydrogen-ion concentration forces back the ionization of $Al(OH)_3$ as an acid. In the second case when a base such as NaOH is added to $Al(OH)_3$ the hydrogen-ion concentration is lowered by neutralization and at the same time the ionization of $Al(OH)_3$ as a base is repressed; to again restore equilibrium, more solid must

dissolve and ionize. Thus in both cases final equilibrium is established when all the solid has dissolved and the ion product of water (1.2×10^{-14}) is maintained.

The tendency for $Al(OH)_3$ to ionize as a base is somewhat more marked than its tendency to ionize as an acid; in other words, a saturated solution of aluminum hydroxide contains slightly more hydroxyl ions than hydrogen ions. With $Zn(OH)_2$ the basic tendency is still more marked; with certain other amphoteric hydroxides the acid tendency predominates.

OTHER EQUILIBRIUM RELATIONSHIPS: GASEOUS-LIQUID AND LIQUID-LIQUID SYSTEMS

The equilibrium conditions existing in solutions containing dissolved gases constitute important cases of equilibria. Reference has already been made (see page 12) to solutions of this type as important laboratory reagents.

The amount of gas which will dissolve in a given amount of water depends upon the nature of the gas and the temperature and pressure. Hydrogen chloride and hydrogen sulfide are two examples of this type. Thus, gaseous hydrogen chloride will dissolve in water up to its limit of solubility, forming the reagent, hydrochloric acid. At ordinary temperatures and pressures " concentrated " HCl solution contains about 37 per cent of hydrogen chloride by weight and this is ionized about 60 per cent. Hydrogen sulfide is much less soluble and forms at room conditions an approximately 0.1 molar solution in which the primary ionization is about 0.05 per cent. Increase of temperature will lower the solubility, and increase in pressure will cause more gas to be dissolved. For these reasons, boiling a solution is often resorted to in order to remove dissolved gases, and the carrying out of certain reactions such as precipitations with H_2S under pressure is advantageous. In systems of this kind, the equilibrium for a saturated solution depends largely on temperature and pressure.

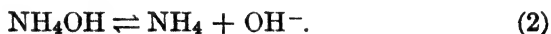
In the cases where the gas is the anhydride, the equilibria become more complicated. Sulfur dioxide, sulfur trioxide and carbon dioxide may be cited as examples. Here must be considered not only the physical equilibrium between the dissolved gas and the solution but also the reaction of the gas with water and the equilibrium of the ions of the product formed in the

reaction. For instance, sulfur trioxide, when passed into water, reacts, since it is an acid anhydride, to form sulfuric acid. This reaction proceeds until concentrated sulfuric acid is formed, that is, until all the water present has reacted. The H_2SO_4 in turn ionizes in two stages. Further passage of SO_3 into the vessel will produce fuming sulfuric acid. Similar relationships hold true for solutions of SO_2 and CO_2 in water, but here the solubilities of the gases are much less.

The Ammonia Equilibrium.—The case of ammonium hydroxide is of especial importance and has already been referred to under ionization of weak electrolytes and again later under complex ion formation. When ammonia is passed into water, a small amount reacts to form ammonium hydroxide, according to the reaction:

$$NH_3 + H_2O \rightleftharpoons NH_4OH. \qquad (1)$$

The ammonium hydroxide, as a weak base, ionizes into NH_4^+ ions and OH^- ions, the extent for a 0.1 molar solution at 18° C. being 1.31 per cent:

$$NH_4OH \rightleftharpoons NH_4 + OH^-. \qquad (2)$$

The equilibrium expression for reaction (1) can be written thus:

$$\frac{C_{NH_3} \times C_{H_2O}}{C_{NH_4OH}} = k,$$

and since the concentration of water is practically constant we can write:

$$\frac{C_{NH_3}}{C_{NH_4OH}} = \frac{k}{C_{H_2O}} = k'. \qquad (3)$$

The value of k' has been found to be 2 at 20° C. The expression gives the proportion of NH_4OH to NH_3 which can exist in solution when NH_3 is passed into water.

For reaction (2), the true ionization constant can be calculated from the expression:

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = k''. \qquad (4)$$

The value of k'' has been found to be 5×10^{-5} and shows the proportion of NH_4OH which has ionized.

The two expressions (equations (3) and (4)) can be combined into a single ratio in the following manner: Rewrite equation (3) in the form:

$$C_{NH_3} = k' \times C_{NH_4OH}$$

and then add the factor C_{NH_4OH} to both sides:

$$C_{NH_3} + C_{NH_4OH} = C_{NH_4OH} \times (k' + 1)$$

$$C_{NH_4OH} = \frac{C_{NH_3} + C_{NH_4OH}}{(k' + 1)}.$$

Substitute this value for C_{NH_4OH} in equation (4):

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_3} + C_{NH_4OH}} = \frac{k''}{(k' + 1)} = K. \qquad (5)$$

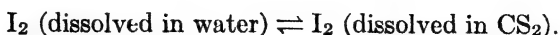
The value for K has been found to be approximately 0.000018 at 18° C. Equation (5) shows that the product of the concentrations of the ions depends upon the concentration of non-ionized ammonium hydroxide as well as the concentration of the dissolved ammonia. We shall have occasion to apply this equilibrium in actual analysis.

THE DISTRIBUTION RATIO

Another type of equilibrium exists for a dissolved substance which distributes itself between two immiscible solvents. If a second solvent is added to a solution, the solute will divide itself between the two solvents in a ratio which is always constant no matter what the absolute amounts of solute may be. This ratio is called the **distribution ratio** or sometimes the **partition coefficient.** Some cases are encountered in qualitative analysis where this relationship is involved. Iodine may be used to illustrate this principle.

When iodine is liberated from an iodide it will dissolve to a small extent in the aqueous solution. If carbon disulfide, which is immiscible with water, is added, a two-liquid-layer system is formed. The iodine is about 400 times more soluble in the CS_2 and most of it will go into the CS_2 layer. An equilibrium will then exist between the I_2 in the water and the I_2 in the CS_2. The equilibrium amounts of I_2 in the two liquids are always such that

their ratio gives an equilibrium constant. This can be expressed algebraically as follows:

$$I_2 \text{ (dissolved in water)} \rightleftharpoons I_2 \text{ (dissolved in } CS_2).$$

As an equilibrium ratio this becomes:

$$\frac{C_{(I_2 \text{ in } CS_2)}}{C_{(I_2 \text{ in water})}} = K_{\text{(distribution ratio)}}$$

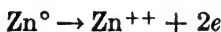
This behavior of iodine is used in the method of testing for iodides. A similar ratio is obtained for bromine. Another example is encountered in the test for chromium.

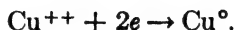
In general, certain separations can be made more complete and certain tests more delicate if we change the solvent. Organic liquids such as alcohol, ether, chloroform, carbon tetrachloride and carbon disulfide are frequently used for this purpose.

ELECTROCHEMICAL THEORY OF OXIDATION-REDUCTION

Attention has already been called, in the section on the writing of equations, to the electrical nature and the transfer of electrons in reactions of oxidation and reduction. Such reactions, like all others taking place in aqueous solutions, reach an equilibrium. It will now be shown how the equilibrium constants for such reactions are calculated and how relative oxidizing and reducing abilities are measured.

The dissolving of a metal, i.e., passing from the solid (atomic) state to the ionic condition, is a simple illustration of an oxidation, as for instance, with zinc:

$$Zn^{\circ} \rightarrow Zn^{++} + 2e$$

the action being accompanied by the loss of two electrons for each ion formed. Conversely, when the ion of a metal gains electrons and is deposited in the metallic condition, the process is one of reduction as in the deposition of copper:

$$Cu^{++} + 2e \rightarrow Cu^{\circ}.$$

The formation of zinc ions, when a strip of zinc is placed in water or in a dilute solution of a zinc salt, will leave the strip negatively charged and the solution positively charged. There is thus set up

a difference of electrical potential at the contact of the metal and its solution. The value of the potential difference depends, among other factors, on the "solution pressure" of the metal tending to drive atoms into solution and on the osmotic pressure acting in the opposite direction to force ions out of solution. Nernst has derived the following equation for this potential difference, E:

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

in which C, the concentration of ions in the solution, is substituted for the osmotic pressure; k is the so-called Nernst constant, substituted for the solution pressure; n is the valence change and 0.059 a constant (here given for 25° C.).

There is no direct way by which the value of E can be determined, but relative values can be obtained by making the strip of metal with its solution one of the electrodes of a voltaic cell, the other electrode being either a standard hydrogen or a standard calomel electrode.

A standard or "normal" hydrogen electrode consists of a small strip of platinum coated with platinum black and joined to a wire encased in a glass tube. The tube is surrounded by another, larger tube through which a stream of hydrogen is passed. This arrangement is placed in a vessel containing acid whose H^+ ion concentration (or, more accurately, its hydrogen-ion activity) is exactly 1. Such an electrode is arbitrarily assigned a potential of zero.

If then a zinc electrode is joined, by an external circuit, through a voltmeter or potentiometer to a hydrogen electrode and the two solutions are connected by means of a tube containing a conducting salt solution, the voltage indicated on the instrument will be the difference between that of the zinc electrode and that of the hydrogen electrode. Since the standard hydrogen electrode potential has been taken as 0, that of the zinc electrode will be the value indicated. In this way it has been found that for a zinc electrode, when the concentration of zinc ions is exactly molar, the potential is -0.76 volt. Similarly, for a copper electrode, the molar potential is $+0.34$ volt. Values for practically all the metallic elements have in this way been determined. When arranged in order, they constitute the familiar potential series or Electro-

motive Series of Metals. The more common metals are incorporated in Table VIII.

The electrode potential is a measure of the ease with which the metal is converted from the atomic to the ionic state. The higher the position of the metal in the series, the more readily it becomes oxidized; the reducing action of the metal decreases as we go down through the series. Since, for example, from the relative positions of zinc and copper in the series, zinc is more easily oxidized than copper, a piece of metallic zinc placed in a solution of a cupric salt will reduce the Cu^{++} ions to metallic copper, the zinc going into solution as Zn^{++} ions and depositing the copper. For the same reason aluminum will deposit antimony, and iron will reduce stannic ions. There are many important applications of this kind in analytical chemistry.

Calculation of Equilibrium Constant.—In the replacement of copper by zinc, the reaction is:

$$Zn^{\circ} + Cu^{++} \rightleftharpoons Zn^{++} + Cu^{\circ}.$$

Applying the Law of Chemical Equilibrium to this reaction, the equilibrium equation becomes:

$$\frac{C_{Zn^{++}} \times C_{Cu^{\circ}}}{C_{Cu^{++}} \times C_{Zn^{\circ}}} = K$$

and equilibrium is reached when the value of K is satisfied. Since the factors $C_{Cu^{\circ}}$ and $C_{Zn^{\circ}}$ represent the solid, metallic condition, they may be considered constant quantities and the above equation becomes simply:

$$\frac{C_{Zn^{++}}}{C_{Cu^{++}}} = K \text{ (Equilibrium constant).}$$

This means that, when the concentration of zinc ions bears a certain ratio to that of the copper ions, the reaction will have reached equilibrium. The equilibrium ratio, i.e., the equilibrium constant K, for this reaction is calculated from electrochemical considerations, using electrode potentials and applying the Nernst equation.

If the strip of zinc is immersed in a solution of a zinc salt and is made one electrode of a voltaic cell, and a strip of copper dipping into a copper salt solution is made the other electrode, the two electrodes joined externally through a voltmeter and internally by

a conducting salt solution, electric current will flow, owing to the passage of electrons from the zinc electrode, through the instrument to the copper electrode. The current will cease when the system has come to equilibrium, and this will occur when the electrode potential of the zinc equals that of the copper.

The Nernst equation:

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

may be expanded into the form:

$$E = \frac{0.059}{n} \log \frac{1}{k} + \frac{0.059}{n} \log C.$$

When the concentration is molar, $C = 1$, and the molar potential E_0 is given by $\frac{0.059}{n} \log \frac{1}{k}$. From this the potential of the electrode for any concentration may be expressed by the equation:

$$E = E_0 + \frac{0.059}{n} \log C.$$

For the zinc electrode:

$$E_{(\text{zinc})} = E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{Zn^{++}}$$

and for the copper electrode:

$$E_{(\text{copper})} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{Cu^{++}}.$$

At equilibrium, when $E_{(\text{zinc})}$ is equal to $E_{(\text{copper})}$,

$$E_{0(\text{zinc})} + \frac{0.059}{2} \log C_{Zn^{++}} = E_{0(\text{copper})} + \frac{0.059}{2} \log C_{Cu^{++}}$$

$$-0.76 + 0.0295 \log C_{Zn^{++}} = 0.34 + 0.0295 \log C_{Cu^{++}}$$

$$1.10 = 0.0295 (\log C_{Zn^{++}} - \log C_{Cu^{++}})$$

$$\log \frac{C_{Zn^{++}}}{C_{Cu^{++}}} = 37.3$$

$$\frac{C_{Zn^{++}}}{C_{Cu^{++}}} = 1 \times 10^{37.3} \quad \text{or} \quad 2 \times 10^{37}$$

$$\therefore \quad K = 2 \times 10^{37}.$$

Therefore, K, the ratio of the Zn^{++} ion concentration to that of the Cu^{++} ion concentration, is 2×10^{37}. This means that, when equilibrium is reached in the reaction in which zinc displaces copper ions, the concentration of Zn^{++} ions is enormous, and the concentration of Cu^{++} ions remaining in solution is negligible; for practical purposes the removal of cupric ions is complete.

When a non-metallic element, such as sulfur or chlorine, dissolves, negatively charged ions (anions) are formed, and the process is one of reduction. For chlorine, for example, the reaction is:

$$Cl_2^{\circ} + 2e \rightleftharpoons 2Cl^-.$$

The Nernst equation for non-metallic electrodes takes the form:

$$E = -\frac{0.059}{n} \log \frac{C_{\text{ion}}}{k}.$$

Since, however, C_{ion}, the concentration of the ion, is dependent upon the solubility of the gas, the equation is transformed into:

$$E = \frac{0.059}{n} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2 \times k}$$

and the molar electrode potential is given by:

$$E_{(Cl)} = E_{0(Cl)} + \frac{0.059}{2} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2}.$$

E_0 for chlorine has been found to be $+ 1.36$ volts. The corresponding value of E_0 for iodine is $+0.54$ volt. (See Table VIII.) The values show chlorine to be a stronger oxidizing agent than iodine and the iodide ion a stronger reducing agent than the chloride ion. Chlorine therefore will oxidize iodides, in accordance with the equation:

$$Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2.$$

The equilibrium constant of this reaction is expressed by the equation:

$$\frac{(C_{Cl^-})^2 \times C_{I_2}}{(C_{I^-})^2 \times C_{Cl_2}} = K.$$

Applying the same electrochemical method as used in determining the Zn^{++}/Cu^{++} ratio, when equilibrium is reached a cell, consisting of a chlorine electrode joined with an iodine electrode,

will show equilibrium when the potentials of the two electrodes are equal. We have then:

$$E_{0(Cl)} + \frac{0.059}{2} \log \frac{C_{Cl_2}}{(C_{Cl^-})^2} = E_{0(I)} + \frac{0.059}{2} \log \frac{C_{I_2}}{(C_{I^-})^2}$$

$$\frac{0.059}{2} \log \frac{C_{I_2}}{(C_{I^-})^2} - \log \frac{C_{Cl_2}}{(C_{Cl^-})^2} = 1.36 - 0.54$$

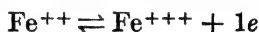
$$\log \frac{(C_{Cl^-})^2 C_{I_2}}{(C_{I^-})^2 C_{Cl_2}} = 27.79$$

$$\log K = 27.79$$

$$K = 1 \times 10^{27.79} \text{ or } 6.3 \times 10^{27}.$$

The value of K shows that the reaction runs very far to completion.

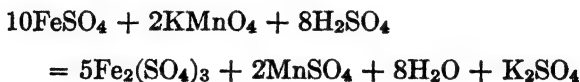
Equilibrium in other Oxidizing-Reducing Systems.—With elements which exist in two different ionic forms such as, for example, the reversible change for the oxidation of ferrous ions and reduction of ferric ions:

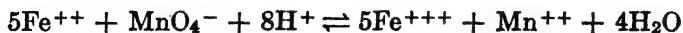
$$Fe^{++} \rightleftharpoons Fe^{+++} + 1e$$

and with the more complex relationships, as in the oxidation of manganous ion and reduction of the MnO_4^- ion in an acidic solution:

$$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e$$

the molar potentials can be determined and the ions arranged into similar series. The more important ones for which data exist are given in Table VIII.

Equilibrium constants for any interaction between an oxidizing substance and a reducing substance can be calculated from electrochemical data. For the reaction:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4$$

rewritten in ionic form:

$$5Fe^{++} + MnO_4^- + 8H^+ \rightleftharpoons 5Fe^{+++} + Mn^{++} + 4H_2O$$

the equilibrium constant is expressed by:

$$\frac{(C_{Fe^{+++}})^5 \times C_{Mn^{++}}}{(C_{Fe^{++}})^5 \times C_{MnO_4^-} \times (C_{H^+})^8} = K$$

TABLE VIII

POTENTIAL SERIES

Electrode Reaction	Molar Potential in Volts
$K \rightleftharpoons K^{+} + 1e$	−2.92
$Ba \rightleftharpoons Ba^{++} + 2e$	−2.8
$Ca \rightleftharpoons Ca^{++} + 2e$	−2.76
$Na \rightleftharpoons Na^{+} + 1e$	−2.71
$Sr \rightleftharpoons Sr^{++} + 2e$	−2.7
$Mg \rightleftharpoons Mg^{++} + 2e$	−1.55
$Al \rightleftharpoons Al^{+++} + 3e$	(−1.34)
$Mn \rightleftharpoons Mn^{++} + 2e$	(−1.)
$Zn \rightleftharpoons Zn^{++} + 2e$	−0.76
$Cr \rightleftharpoons Cr^{+++} + 3e$	−0.51
$S^{-} \rightleftharpoons S + 2e$	−0.51
$Fe \rightleftharpoons Fe^{++} + 2e$	−0.44
$Cd \rightleftharpoons Cd^{++} + 2e$	−0.40
$Co \rightleftharpoons Co^{++} + 2e$	(−0.26)
$Ni \rightleftharpoons Ni^{++} + 2e$	(−0.25)
$Sn \rightleftharpoons Sn^{++} + 2e$	−0.14
$Pb \rightleftharpoons Pb^{++} + 2e$	−0.13
$Fe \rightleftharpoons Fe^{+++} + 3e$	−0.04
$H_2 \rightleftharpoons 2H^{+} + 2e$	0.00
$Sn \rightleftharpoons Sn^{++++} + 4e$	+0.05
$Cu \rightleftharpoons Cu^{++} + 1e$	+0.17
$Sn^{++} \rightleftharpoons Sn^{++++} + 2e$	+0.2
$Sb \rightleftharpoons Sb^{+++} + 3e$	(+0.2)
$Bi \rightleftharpoons Bi^{+++} + 3e$	(+0.2)
$As \rightleftharpoons As^{+++} + 3e$	(+0.3)
$Cu \rightleftharpoons Cu^{++} + 2e$	+0.34
$4OH^{-} \rightleftharpoons O_2 + 2H_2O + 4e$	+0.40
$Co \rightleftharpoons Co^{+++} + 2e$	+0.42
$Fe(CN)_6^{--} \rightleftharpoons Fe(CN)_6^{=} + 1e$	+0.44
$Cu \rightleftharpoons Cu^{+} + 1e$	+0.52
$MnO_2 + 4OH^{-} \rightleftharpoons MnO_4^{-} + 2H_2O + 3e$	+0.54
$2I^{-} \rightleftharpoons I_2 + 2e$	+0.50
$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^{+} + 2e$	+0.58
$Fe^{++} \rightleftharpoons Fe^{+++} + 1e$	+0.76
$2Hg \rightleftharpoons Hg_2^{++} + 2e$	+0.8
$Ag \rightleftharpoons Ag^{+} + 1e$	+0.81
$Hg^{++} \rightleftharpoons Hg^{++} + 2e$	+0.86
$Hg_2^{++} \rightleftharpoons 2Hg^{++} + 2e$	+0.9
$NO + 2H_2O \rightleftharpoons NO_3^{-} + 4H^{+} + 3e$	+0.95
$2Br^{-} \rightleftharpoons Br_2 + 2e$	+1.07
$Au^{+} \rightleftharpoons Au^{+++} + 2e$	+1.2
$Cr^{+++} + 4H_2O \rightleftharpoons HCrO_4^{-} + 7H^{+} + 3e$	+1.3
$2Cl^{-} \rightleftharpoons Cl_2 + 2e$	+1.36
$Au \rightleftharpoons Au^{+++} + 3e$	+1.38
$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^{-} + 8H^{+} + 5e$	+1.50

THE STRUCTURE OF COMPOUNDS

Determining the nature of chemical union is one of the most fundamental problems in chemistry. Since the introduction of the electron into chemistry the problem has become, to a great extent, one of showing how the electron functions in forming chemical bonds, i.e., in producing what we call valence. The explanation of valence in terms of electrons is, in its simple aspects, so easily understood and has been so successful in explaining many chemical facts that it is now introduced into practically every elementary course in chemistry. For this reason some of the following discussion will be familiar to the student; it is repeated here to serve as a review and as an introduction to less familiar material.

THE STRUCTURE OF THE ATOM AND THE NATURE OF VALENCE

An atom may be visualized as a miniature solar system. A small, very dense nucleus takes the place of the sun, and a number of electrons, sometimes called negatrons, move about it after the fashion of planets. The nucleus is positively charged, and the number of planetary electrons is equal to the number of units of charge on the nucleus, that is, the atomic number. The nucleus provides practically all the mass of the atom and is itself quite complex in structure, but for the present purpose this need not concern us.

Each planetary electron is characterized by a set of four quantum numbers which describe its energy state. The values of these quantum numbers are subject to certain limitations, and there is an important restriction to the effect that no two electrons in the same atom can have the same set of four quantum numbers, although they may have one, two or three the same. Electrons which have the same value of a certain one of them, called the principal or total quantum number, n, form a group, the maximum number of electrons in which, owing to the limitations referred to above, is definite and is equal to $2 \times n^2$. Such a group is often called an orbit, ring or shell of electrons. By assigning values 1, 2, 3, 4, etc., to n it is seen that successive groups may contain a maximum of 2, 8, 18, 32, etc., electrons. Within each of these groups, after the first, there are subgroups made up of electrons which have two quantum numbers, one of them n, the same. The

number of electrons in such subgroups follows the series 2, 6, 10, 14, etc. Thus, the group 8 is made up of subgroups 2, 6; 18 is made up of subgroups 2, 6, 10; and so on. Further consideration of the quantum numbers is unnecessary for our purpose.

For each of the ninety-two elements a distribution of the electrons may be made among the above-mentioned groups and subgroups. The group having the highest value of n is often called the valence group or valence orbit, and it determines to a large extent the chemical behavior of the element. In connection with this group the number 8 is extremely significant, as is apparent when we realize that the presence of eight electrons in the group gives a stable, chemically inactive atom, regardless of the maximum number that the group may contain. If the highest value of n in the atom is 1, it is, of course, impossible to have eight electrons in the valence shell, but in this case 2 is the number that gives stability. In the table below is given the electronic configuration of each of the inert gases as well as of some of the more familiar elements. (The numbers in the table are the number of electrons in each of the orbits, i.e., electrons having the same value of n, the principal quantum number.) It will be noted that each of the inert gases, except helium, has a stable group of eight electrons in the valence orbit, and that no other element has such an arrangement.

Atoms of elements which do not have a stable valence group like that of one of the inert gases have a tendency to attain such a configuration, and their chemical properties are largely determined by the magnitude of the tendency and the manner of attaining the configuration. An atom may secure a stable valence group in either of two general ways:

1. By capturing from one or more atoms enough electrons to make a total of eight in the valence group, or by losing to other atoms all the electrons in its own valence group. In the latter case the atom reverts to the next lower stable configuration.
2. By sharing electrons with another atom or with each of several other atoms, each electron so shared being counted in the valence group of each of the two atoms involved in the sharing.

If a stable group is formed, as indicated in 1, by capturing or

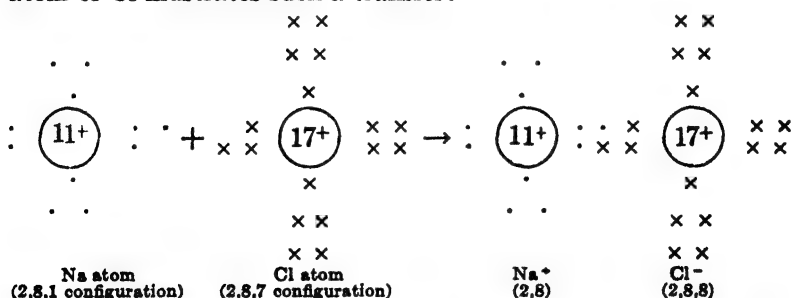
TABLE IX

VALUES OF n

Element	1	2	3	4	5	6	7
Hydrogen......	1						
Helium.........	2						
Lithium........	2	1					
Oxygen.........	2	6					
Fluorine........	2	7					
Neon..........	2	8					
Sodium........	2	8	1				
Chlorine........	2	8	7				
Argon..........	2	8	8				
Iron............	2	8	14	2			
Bromine........	2	8	18	7			
Krypton........	2	8	18	8			
Silver..........	2	8	18	18	1		
Iodine.........	2	8	18	18	7		
Xenon.........	2	8	18	18	8		
Lead...........	2	8	18	32	18	4	
Radon..........	2	8	18	32	18	8	
Radium........	2	8	18	32	18	8	2

losing electrons, there is an actual transfer of electrons from one atom to another. This transfer leaves the donor atoms positively charged and gives the acceptor atoms a negative charge, forming cations and anions, respectively. The following equation for the formation of a molecule of NaCl from an atom of Na and an atom of Cl illustrates such a transfer:

$$(11^+) \quad + \quad (17^+) \quad \rightarrow \quad (11^+) \quad (17^+)$$

Na atom (2,8,1 configuration)	Cl atom (2,8,7 configuration)	Na^+ (2,8)	Cl^- (2,8,8)

This representation is not to be interpreted too literally. The use of different symbols to represent the electrons belonging to the sodium and to the chlorine does not indicate any difference

in the electrons; the purpose is merely to simplify the visualization of the electron transfer. Also, the distribution about the atom is not intended to represent the spatial relations of the electrons to the nucleus in an actual atom; it is simply a means of representing pictorially the successive electronic groups and the number of electrons in each group.

It will be noticed that the single electron in the valence shell of the sodium atom has been transferred to the valence shell of the chlorine atom, forming a sodium ion and a chloride ion, each of which has a stable group of eight electrons in the outer group. A crystal of NaCl is an aggregate of such ions. It should be emphasized that in compounds of this type the ions are not formed upon dissolving the material but are already present in the solid compound.

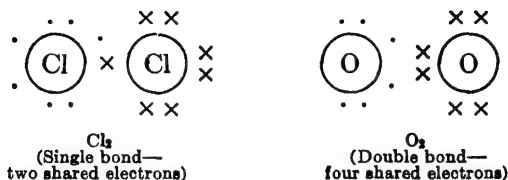
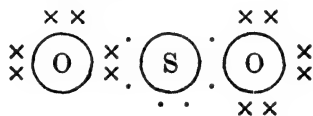
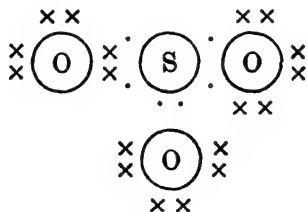
A valence bond formed in this way is called a polar, heteropolar or ionized bond, and this type of valence is called polar valence, electrovalence or ionized valence. Each electron transferred gives one unit of polar valence to each of the two atoms concerned in the transfer, and the number of such units per atom constitutes the electrovalence of the element.

The electropositive elements are those in which the tendency to lose electrons is greater than the tendency to gain electrons in securing a stable group. This is the situation, in general, when the number of electrons in the valence group is less than four as it is in most of the metals. If the tendency to gain electrons is greater than the tendency to lose them the element is electronegative. This happens, in general, when there are six or seven electrons in the valence group, as in many of the non-metals. Elements which have four or five electrons in the valence group, as well as some elements with three or six, or some other number, show, in general, little tendency either to gain or lose electrons, and hence rarely form ionized compounds.

Attainment of a stable group by sharing electrons, as indicated in 2, results in the formation of covalent or coordinate covalent bonds. Covalent bonds are sometimes called non-polar or homopolar bonds, and coordinate covalent bonds are sometimes called semipolar or, frequently, simply coordinate bonds. Each pair of shared electrons may be considered to constitute a single bond. In a covalent single bond one of the two shared electrons comes from each of the two atoms. This is illustrated by the following

diagrams of the chlorine and oxygen molecules. For simplicity, all the electrons except those in the valence group have been omitted in these and all subsequent atomic diagrams.

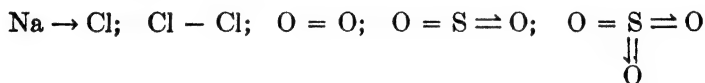
Cl_2
(Single bond—
two shared electrons)

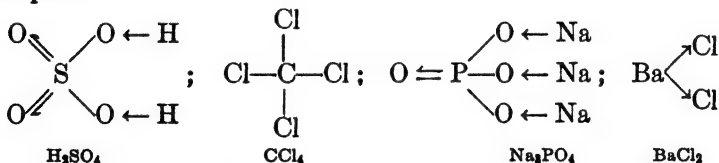
O_2
(Double bond—
four shared electrons)

If, instead of each atom supplying one of the shared electrons, both of the electrons come from the same atom, the result is a coordinate covalent bond and each pair of electrons so shared constitutes one unit of coordinate covalence or one coordinate valence. This is illustrated in the following diagram of SO_2:

The oxygen atom shown on the right in this diagram is joined to the sulfur by a coordinate covalent bond; the one on the left is joined by a covalent double bond. It will be noted that the sulfur atom has another pair of unshared electrons which, presumably, should be able to form a coordinate covalent bond with another oxygen atom. In the SO_3 molecule this additional bond is formed, as is shown in the following diagram:

The diagram of the SO_2 molecule shows that more than one type of valence bond may exist in the same molecule and indicates the difficulty of stating the " valence " of an element or group unless the type of valence concerned is specified.

Thus, while sulfur in SO_2 is usually considered to have a

" valence " of 4, this valence really consists of a covalence of 2 and a coordinate covalence of 1. For convenience, the number 4 may be called the "apparent valence" or "valence number" of sulfur in SO_2, and similarly for other cases.

For simplicity of representation symbols are used to indicate the different types of valence bonds. To indicate a polar bond an arrow is used, the tail of the arrow being placed at the atom that has lost the electron and the head at the atom that has gained the electron. A covalent bond is represented by a straight line. A coordinate covalent bond is designated by the combination of an arrow and a straight line: $\rightleftharpoons$; this symbol indicates that a coordinate covalent bond may be considered as made up of a polar and a covalent bond, hence the term semipolar which is sometimes applied to it. We may look upon such a bond as being formed by the transfer of one electron from the electron pair of the donor atom, forming a polar bond, and then a sharing of this transferred electron with the electron left behind on the donor atom, forming a covalent bond. If the formulas previously given are rewritten using this notation we get the following less cumbersome representation:

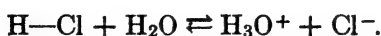
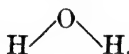
$$\mathrm{Na} \rightarrow \mathrm{Cl}; \quad \mathrm{Cl} - \mathrm{Cl}; \quad \mathrm{O} = \mathrm{O}; \quad \mathrm{O} = \mathrm{S} \rightleftharpoons \mathrm{O}; \quad \begin{array}{c} \mathrm{O} = \mathrm{S} \rightleftharpoons \mathrm{O} \\ \downharpoonleft\!\mid \\ \mathrm{O} \end{array}$$

It would be valuable practice for the student to construct the electronic diagrams of other compounds, such as the following examples:

$$\begin{array}{c} \begin{array}{ccc} \mathrm{O} & & \mathrm{O} \leftarrow \mathrm{H} \\ & \mathrm{S} & \\ \mathrm{O} & & \mathrm{O} \leftarrow \mathrm{H} \end{array} \\ H_2SO_4 \end{array} ; \quad \begin{array}{c} \begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl}-\mathrm{C}-\mathrm{Cl} \\ | \\ \mathrm{Cl} \end{array} \\ CCl_4 \end{array} ; \quad \begin{array}{c} \begin{array}{l} \quad\quad\;\; \mathrm{O} \leftarrow \mathrm{Na} \\ \mathrm{O} \rightleftharpoons \mathrm{P}-\mathrm{O} \leftarrow \mathrm{Na} \\ \quad\quad\;\; \mathrm{O} \leftarrow \mathrm{Na} \end{array} \\ Na_3PO_4 \end{array} ; \quad \begin{array}{c} \mathrm{Ba}\begin{array}{l} \nearrow \mathrm{Cl} \\ \searrow \mathrm{Cl} \end{array} \\ BaCl_2 \end{array}$$

The student must again be cautioned not to interpret such diagrams too strictly. The diagram of Na_3PO_4, for example, seems to indicate some sort of a definite relationship between each of the sodium ions and a particular one of the oxygen atoms; also it would seem to indicate that one of the oxygen atoms plays a rôle in the structure of the molecule which is different from that played by the other three. It is probable, however, that neither of these suppositions is correct. Studies of crystal structure show

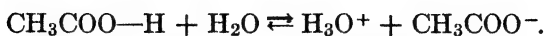
that in the solid form this compound consists, as might be supposed, of Na^+ ions and of the $PO_4^{\equiv}$ group. In the latter group the oxygen atoms are symmetrically arranged about the central phosphorus atom, and all four appear to be identical in their relationship to the central atom and to the sodium ions. It is perhaps more accurate, therefore, to consider the transfer of three electrons from sodium atoms to the PO_4 group, without attempting to designate the specific atoms that have gained those electrons.

When a substance containing polar bonds is dissolved in a polar solvent, such as water, the polar bonds are broken and the ions move about more or less independently of each other. This is equivalent to saying that compounds having polar bonds are completely ionized in solution, as they are in the solid state. On the other hand, covalent and coordinate covalent bonds are broken, in general, only to a slight extent, if at all. This means that atoms which are held together by shared electron bonds will usually remain intact and act as a unit in solution, and the fact that the sulfate, phosphate and similar ions act as units in many chemical reactions may be explained on this basis.

Although a compound may contain no polar bonds and thus be undissociated or non-ionized in the pure condition, it may nevertheless be considerably ionized when dissolved in a polar solvent, such as water, owing to the attraction of the polar solvent molecules for one or another of the atoms of the compound. An example of this is hydrogen chloride, H—Cl, which in the gaseous state contains no polar bond. However, when it is dissolved in water, the water molecule, as a result of its polarity, exerts a strong attraction on the hydrogen atom of the HCl molecule. This attraction is so strong that the hydrogen is pulled away from the chlorine, but both of the shared electrons remain behind with the chlorine. According to the classical theory of ionization, a simple H^+ ion is produced (see page 11), but on the basis of the above conception, an H_3O^+ ion is formed. Such a process may be represented by the equation:

$$H{-}Cl + H_2O \rightleftarrows H_3O^+ + Cl^-.$$

A similar action is involved in other ionization processes, especially those in which a weak electrolyte is involved. Thus, acetic acid contains no polar bond, but in water solution it ionizes to a slight extent, much less than HCl, and according to the classical view-

point yields H^+ and $C_2H_3O_2^-$ ions but here is represented by the equation:

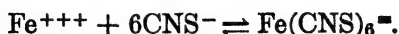
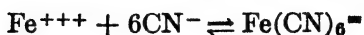
$$CH_3COO—H + H_2O \rightleftarrows H_3O^+ + CH_3COO^-.$$

The different degrees of ionization of various compounds containing no polar bonds may be explained by assuming that the attractive forces tending to hold the solute molecules together are not of the same magnitude in all the compounds; the less the attractive forces the easier it is for the attraction of the solvent molecules to pull the solute molecules apart, that is, the greater the degree of ionization.

To avoid confusion it may be well to point out the fact that a polar molecule does not necessarily contain a polar valence bond. Thus, H_2O and NH_3 are both polar molecules but neither contains any but covalent bonds. The polarity is due to the unsymmetrical nature of the molecule. The water molecule, for example, is not correctly represented by H—O—H but rather by H/O\H, in which the valence bonds of the two hydrogen atoms make an angle of approximately 100° with each other. For this reason the " center of gravity " of the positive charge of the molecule does not coincide with the " center of gravity " of the negative charge, as it would if the three atoms were in a straight line, so the molecule acts as a tiny magnet, i.e., it is a polar molecule.

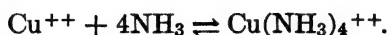
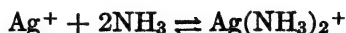
Complex Ions and Complex Compounds.—The term complex ion is used differently by different authors. It is sometimes applied to any ion made up of atoms of two or more elements, but this usage is generally limited to include only the less familiar ions, thus eliminating such common groups as $SO_4^=$, $PO_4^{\equiv}$, NO_3^-, ClO_3^-, etc. An ion is especially likely to be eliminated on the basis of common occurrence if, like those mentioned above, it shows little or no tendency to dissociate into simpler ions or compounds. In this discussion we shall mean by the term complex ion an ion that is more or less readily formed by the combination of an ion with one or more other ions or neutral molecules. This will exclude such ions as those mentioned above, and they will be designated as compound ions. Examples of the formation of complex ions are the following:

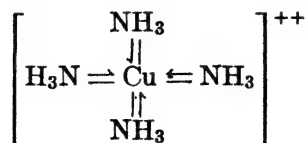
Combination of an ion with other ions:

$$Fe^{+++} + 6CN^{-} \rightleftharpoons Fe(CN)_6^{\equiv}$$

$$Fe^{+++} + 6CNS^{-} \rightleftharpoons Fe(CNS)_6^{\equiv}.$$

Combination of an ion with neutral molecules:

$$Ag^{+} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^{+}$$

$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{++}.$$

Covalence and, especially, coordinate covalence are important in the discussion of complex ions because it is by means of these two types of bonds that the parts of a complex ion are held together. To get some idea of the nature of this binding we may use for a simple example the intensely blue complex ion formed by adding a solution of NH_3 to a solution of a copper salt, a reaction with which the student is probably familiar. The copper ion as it exists in the original solution has, of course, no electrons in the valence shell. The nitrogen atom in NH_3 has shared three of its five electrons with three hydrogen atoms, giving it a total of eight electrons in its valence shell, and leaving a pair of electrons not shared with any atom. The NH_3 molecule accordingly shares this pair of electrons with the Cu^{++} ion, and a similar action on the part of three other NH_3 molecules gives the ion a stable group of eight electrons in its valence shell while still retaining its original charge. The condition in which the ion has a valence group of eight electrons appears to be a more stable arrangement than that in which the valence group is entirely absent, so the complex ion is a relatively stable ion. We may represent the complex ion as follows:

$$\left[\begin{array}{ccc} & NH_3 & \\ & \downarrow\downarrow & \\ H_3N \rightrightarrows & Cu & \leftleftarrows NH_3 \\ & \uparrow\uparrow & \\ & NH_3 & \end{array}\right]^{++}$$

The NH_3 molecule when combined in a complex ion is called the ammine group, so this ion is properly called the cupric-tetrammine ion. Unfortunately, however, the terms cupric-ammonia or cupric-ammonium ion are still widely used.

A statement similar to the above may serve to explain the structures of very many complex ions and hydrates, the latter being, at least in many instances, a type of complex ion. A difficulty arises in cases like $Ag(NH_3)_2^+$ and $Co(NH_3)_6^{+++}$ where, following the same general line of thought, it would appear that there are, respectively, two and six coordinate covalent bonds and hence four and twelve electrons in the valence groups of the silver and cobalt, whereas we have been led always to expect a stable group of eight. This difficulty may be resolved, but not without damage to the apparent simplicity of the preceding discussion, by assuming (1) that the stable group need not always consist of eight electrons but may at times, depending largely upon the relative sizes of the atoms or groups concerned, be any even number from four to sixteen, eight and twelve being by far the most common, or (2) that a single electron or even three electrons, instead of the usual two, may sometimes form a bond. Each of these possibilities has evidence in its favor, but as yet there is no way of knowing which, if either, is the correct explanation or whether both may be right.

The Werner Theory of Valence.—In the compound $CuSO_4$ the copper was formerly considered to have a " valence " of positive two and the sulfate to have a " valence " of negative two. On this basis alone, it is obviously impossible to explain the formation of the compound $Cu(NH_3)_4SO_4$ from a supposedly " neutral " molecule of $CuSO_4$ and supposedly neutral NH_3 molecules. Likewise other complex compounds are formed with complete disregard for the traditional rules of valence. This difficulty was recognized many years ago but was completely unresolved until Werner, in 1891, long before the development of the electronic theory of valence, introduced a theory which systematized the study of such compounds and to a large extent explained their structure and behavior.

Werner postulated the existence of two types of valence: (1) primary valence, by means of which the copper and the sulfate, in the above example, are held together, and (2) secondary, auxiliary or coordinate valence by means of which " neutral " molecules such as NH_3 may be joined to other neutral molecules without affecting the primary valences in the molecules so joined. It is the primary valence of Werner that has been traditionally known as the valence of an element or radical.

Werner assigned a definite secondary valence to an element or radical, the value depending upon the number of molecules such as NH_3 which could combine with one atom of the element or a single one of the groups. Just as some elements may have a variable primary valence, so also they may have a variable secondary valence. The number of units of secondary valence is called the coordination number of the atom exhibiting the valence; thus, in $Cu(NH_3)_4SO_4$ the coordination number of copper is 4. The values of the coordination number range from 2 to 8, with 4 and 6 by far the most frequent in occurrence. The combination of the central atom and the groups attached to it by secondary valence bonds is called the coordinated group and is distinguished from the rest of the molecule by enclosing it in brackets, e.g., $[Cu(NH_3)_4]SO_4$. Werner used a dotted line to indicate a secondary valence bond, and this representation is still in common use.

The idea of secondary valence was very extensively developed by Werner and by others. It was discovered that the maximum value of the coordination number may be closely correlated with the position of the element in the periodic table, the maximum value increasing with increase in the atomic number of the element. This would seem to indicate a dependence of the coordination number on the size of the central atom, which would suggest some sort of a regular geometrical arrangement of the coordinated molecules about the central atom. Considerable evidence indicates that this is a correct interpretation.

The student has undoubtedly noted by this time the similarity between Werner's primary valence and the polar valence of the electronic theory as well as between his secondary valence and what we have described previously as coordinate covalence. This is more than an accidental resemblance; in fact, they are essentially the same theory expressed in different terms. The relationship may be made still more apparent by considering a few more aspects of Werner's theory.

An important feature of the theory is that it is possible for a singly charged anion to take the place of one of the neutral molecules in the coordinated group, but when this occurs the charge on the coordinated group is changed by an amount equal to the charge on the replacing ion. Any ion so included in the coordinated group loses many of its characteristic properties,

chloride ion, for instance, no longer being precipitated when silver nitrate is added.

We may now see the application of the above feature to some specific compounds. For this purpose we may use for the central atom trivalent cobalt which has a coordination number of 6 and, as will be learned later, forms a great number of complex ions. The complex ion formed with ammonia should have the formula $[Co(NH_3)_6]^{+++}$, but this happens to be only one of a series of complex ions containing cobalt and ammonia. This series is of no particular importance in itself so far as we are concerned, but it illustrates so well the range of possibilities in the formation of such ions that we may be justified in examining it in some detail.

If we consider the $[Co(NH_3)_6]^{+++}$ ion and replace the ammonia molecules one by one by a monovalent anion which we may designate by X, ions of the following compositions and charges will be obtained: $[Co(NH_3)_5X]^{++}$, $[Co(NH_3)_4X_2]^{+}$, $[Co(NH_3)_3X_3]^{\circ}$, $[Co(NH_3)_2X_4]^{-}$, $[Co(NH_3)X_5]^{=}$, $[CoX_6]^{\equiv}$. Many compounds containing the above ions, X being Cl, NO_3, $\frac{1}{2}SO_4$ or some similar group, have been prepared. The changes in color of cobalt solutions when ammonium hydroxide is added (page 157) may be interpreted as being due to a change from one to another of the above ions.

The explanation of the formation of this series of compounds on the basis of the electronic theory is relatively simple. In the $[Co(NH_3)_6]^{+++}$ ion the cobalt atom has a coordination number of 6, i.e., six pairs of electrons have been shared with it, one pair coming from each of the six NH_3 molecules. If, by some means, one of these NH_3 molecules were to be removed from the coordinated group, taking with it both of the shared electrons, the Co atom would have an unsatisfied secondary valence, that is, an incomplete group of electrons, and would be in a position to form another coordinate covalent bond with some other molecule or ion. The chloride ion, for example, having four pairs of electrons not shared with any atom, is able to supply the two electrons needed by the cobalt, and accordingly enters the coordinated group. However, since the chloride ion carries one unit of negative charge, the net charge of the coordinated group is lowered by this amount, giving the formula $[Co(NH_3)_5Cl]^{++}$. Also, since the chloride ion is now attached by means of a coordinate covalent bond it is no longer able to give the reactions characteristic of the

ion; for instance, it is not precipitated as AgCl when $AgNO_3$ is added. By a repetition of the above process, until finally no more NH_3 molecules remain in the coordinated group, each of the other ions may be formed.

Throughout this discussion we have been speaking of ions, but it has probably been noted that one member of the series is not an ion but an unionized compound. Compounds of this type, e.g., $[Co(NH_3)_3(NO_3)_3]$, are those in which there have been introduced just enough negatively charged ions to compensate for the positive charge of the original ion, leaving the entire coordinated group uncharged or unionized and hence analogous to unionized organic compounds such as chloroform. Such unionized organic compounds are usually insoluble in water but soluble in ether or alcohol, distillable, and rather inert chemically; and compounds of the above type, even though they may be purely inorganic, are analogous in many points of behavior to the unionized organic compounds.

A great variety of compounds containing complex ions such as those described for cobalt may be formed by many of the metals, especially those in the eighth column of the periodic table. It should, perhaps, be pointed out that a number of different groups may be included in the coordinated group; thus coordinated groups such as $[Co(NH_3)_2(H_2O)_2ClBr]^+$ and others tremendously more complicated are entirely possible and compounds containing them have been prepared, but such complications need not concern us here. We should notice, however, that the ferricyanide ion, $Fe(CN)_6^{\equiv}$, may be rewritten as $[Fe(CN)_6]^{\equiv}$ which is now exactly analogous to the $[CoX_6]^{\equiv}$ ion in the series previously discussed, indicating that the iron has a primary valence of 3 and a secondary valence of 6 or, in other words, the ferric ion has formed coordinate covalent bonds with six CN^- ions. In a similar way the structure of ferrocyanides and other complex cyanides, including those such as sodium nitroprusside, $[Fe(NO)(CN)_5]Na_2$, may be explained.

So far we have considered only purely inorganic complex ions. There are, however, many organic molecules, such as urea, pyridine, ethylenediamine, hexamethylenetetramine and many others, which readily enter the coordinated group and give rise to the so-called metallo-organic compounds. Many of these organic compounds contain nitrogen, and it can be shown that usually,

if not invariably, there is an unshared pair of electrons on the nitrogen atom by means of which a coordinate covalent bond may be formed with the central atom. The compounds that do not contain nitrogen can also be shown to possess such an unshared electron pair at some point in the molecule. By making electronic diagrams, the student may prove to himself that the groups $-\overset{\overset{\displaystyle O}{\|}}{C}-$ and $=N-O-H$, for example, always contain such a pair on the oxygen and nitrogen atoms, respectively.

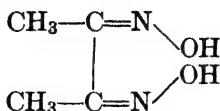
Such organic compounds as tartaric acid, citric acid and sugars interfere with the normal reactions of iron, cobalt and other metals. Examination of the formulas of these substances will show that each contains several $-\overset{\overset{\displaystyle O}{\|}}{C}-$ groups, indicating that it is possible for them to enter the coordinated group of the metal, forming complex ions and thus, as would be expected, giving a behavior different from that usually attributed to the metallic ion itself. The formation of such complex ions may, if they are distinctively colored, serve as a qualitative test for the metal ion. Examples of this sort will be found in the descriptions of the reactions of the metals.

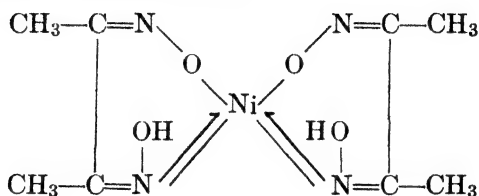
Chelate Compounds.—So far in the discussion of complex ions and compounds we have mentioned only those in which a molecule in the coordinated group has only one point of attachment to the central atom. It is perfectly possible, however, for the same molecule to be attached to the central atom at two different points, thus forming a ring structure. Compounds having such a structure have been called inner complex compounds or chelate compounds, the word chelate, meaning "claw-like," suggesting the manner in which the molecule is attached to the central atom.

The molecule may be attached to the central atom by two covalent bonds, by one covalent and one coordinate covalent bond or by two coordinate covalent bonds. Of these three possibilities only the latter two will be considered here, and we shall make no effort to distinguish between them, although it is possible to do so. The nature of these chelate compounds is best explained by consideration of a specific example.

Nickel, which commonly has a primary valence of 2 and a

coordination number of 4, forms with α-dimethylglyoxime (see page 155),

```
CH3—C=N
    |    \OH
    |    /OH
CH3—C=N
```

a compound having the structure:

```
CH3—C=N                 N=C—CH3
    |   \              /    |
    |    O            O     |
    |     \          /      |
    |       Ni
    |   OH   //    \\   HO  |
    |   |  //        \\  |  |
CH3—C=N                 N=C—CH3
```

It will be noticed that each of the two organic molecules is attached to the nickel at two points, forming two six-membered rings, that is, a chelate compound. It is seen that nickel has taken the place of a hydrogen atom in each of the two organic molecules, forming covalent bonds with the oxygen atoms to which the hydrogen was originally attached. The originally unshared pair of electrons on the nitrogen atoms of the other two $= N - OH$ groups now form two coordinate covalent bonds with the nickel. From the stated valences of nickel it is apparent that the compound $[Ni(NH_3)_2X_2]$, if it exists, should be unionized and should have properties of the sort described for $[Co(NH_3)_3X_3]$ (page 98). This unionized nickel compound has two covalent and two coordinate covalent bonds, which is exactly the situation existing in the α-dimethylglyoxime compound. The latter should, then, have the properties of such unionized molecules, and this is actually so, for the compound is insoluble in water but soluble in pure ethyl alcohol and may be sublimed without appreciable decomposition.

Dyeing with the use of a mordant, and analytical tests depending upon such a process, may also be explained as being due to the formation of chelate compounds. The aluminon test for aluminum (page 149) illustrates this. When aluminon, a red dyestuff, is added to an acidic solution containing aluminum, the red color is distributed uniformly throughout the solution. The addition of NH_4OH to this solution results in the formation of clumps of $Al(OH)_3$ which are colored bright red by the dye. The dye

collects on the precipitate, leaving the solution practically colorless. Dyes which behave in this way may be shown to have groups that favor the formation of chelate compounds, and although frequently the actual structure of the colored material is totally unknown, it is highly probable that it is a chelate compound.

A material like $Al(OH)_3$ which combines with a dye and forms a stable colored complex is called a mordant, and the combination of a mordant and a dye is called a lake. Lakes are frequently described as being adsorption complexes, but it is probable that, in this case at least, " adsorption " is to be interpreted as an actual chemical combination.

By far the greatest number of chelate compounds have rings containing five or six atoms. A ring of this size seems to give greater stability than one containing less than five or more than six atoms. Students of organic chemistry will recognize this fact as further evidence in support of the Baeyer strain theory of ring formation.

Although the chelate compounds that are of the greatest importance in analytical chemistry are those that are insoluble in water, it must not be supposed that all of them are insoluble. On the contrary, such soluble materials as the complex compounds formed by iron and cobalt with tartrates and citrates (page 202) are probably chelate compounds.

PART II

REACTIONS OF THE CATIONS

The chemical elements for whose detection provision is made in this manual are shown in bold-face type in the Periodic Table in the appendix. According to this arrangement, the elements occupying positions toward the left of the table are the base-forming elements; they form the typical hydroxides, in the elementary state they are metallic in character and when their salts are dissolved in an aqueous medium they exist as positively charged ions or cations. Elements occupying the middle portions of the table are less basic in character and may even show acidic properties; they are the typical amphoteric elements, and their salts may ionize to give both the cation and the anion form of ion. Toward the right of the table are the elements showing strongly acidic properties; they form the strong acids and in the ionized form are typical anions. There are some exceptions to these general rules, notably with regard to iron, nickel, and cobalt.

Cations.—Below is the list of cations for which methods of separation and identification are given, the listing following the order in which the elements are found in the Periodic Table:

The alkali metals, sodium (Na^+); potassium (K^+).

Copper in cupric salts (Cu^{++}); silver (Ag^+).

The alkaline earth metals, magnesium (Mg^{++}); calcium (Ca^{++}); strontium (Sr^{++}); barium (Ba^{++}).

Zinc (Zn^{++}); cadmium (Cd^{++}); mercury in mercurous salts (Hg_2^{++}) and in mercuric salts (Hg^{++}).

Aluminum (Al^{+++}).

Lead (Pb^{++}); tin in stannous salts (Sn^{++}) and in stannic salts (Sn^{++++}).

Arsenic in arsenious salts (As^{+++}) and in arsenic salts (As^{+++++}); antimony (Sb^{+++} and Sb^{+++++}); bismuth (Bi^{+++}).

Nitrogen in the form of the ammonium radical (NH_4^+).

Chromium in chromic salts (Cr^{+++}).

Manganese in manganous salts (Mn^{++}).

Iron in ferrous salts (Fe^{++}) and in ferric salts (Fe^{+++}); nickel (Ni^{++}); and cobalt (Co^{++}).

Anions.—The elements studied under the reactions of the anions are:

The halogens, fluorine, chlorine, bromine and iodine in fluorides (F^-); chlorides (Cl^-); bromides (Br^-) and iodides (I^-).

Sulfur in the form of sulfides ($S^=$); sulfites ($SO_3^=$); thiosulfates ($S_2O_3^=$) and sulfates ($SO_4^=$).

Chromium in chromates ($CrO_4^=$) and in dichromates ($Cr_2O_7^=$).

Nitrogen in nitrites (NO_2^-) and in nitrates (NO_3^-).

Phosphorus in phosphates ($PO_4^\equiv$).

Arsenic in arsenites ($AsO_3^\equiv$) and in arsenates ($AsO_4^\equiv$).

Carbon in carbonates ($CO_3^=$) and in the organic radicals, viz., oxalates ($C_2O_4^=$); acetates ($C_2H_3O_2^-$) and tartrates ($C_4H_4O_6^=$).

Silicon in silicates ($SiO_3^=$).

Boron ($B_4O_7^=$, BO_2^-, $BO_3^\equiv$).

To this list are added the cyanogen radicals: thiocyanates (CNS^-); ferricyanides ($Fe(CN)_6^\equiv$); ferrocyanides ($Fe(CN)_6^{==}$) and cyanides (CN^-).

The Analytical Grouping of the Cations

In the analysis of substances of unknown composition, the cations are detected separately from the anions. That is, one portion of the sample is utilized for the cation analysis and other portions for the anion analysis. As already remarked, although individual reagents which yield specific tests for certain cations have been discovered, the methods of cation analysis recommended here are based on separation of the cations into groups and subgroups. This grouping follows, in general, the conventional macro schemes. The division of the cations into five analytical groups, as worked out under the microtechnique by the use of the several group reagents, is based on the following behavior.

1. If a few drops of hydrochloric acid are added to a mixture of all of the cations, precipitates of silver chloride, AgCl, mercurous chloride, Hg_2Cl_2, and lead chloride, $PbCl_2$, will form. Centrifuging or filtering off these chlorides will separate the silver, the

mercurous mercury and most of the lead from the remaining cations. Ag^+, Hg_2^{++} and Pb^{++} make up **Group I, known as the Hydrochloric Acid Group** or the **Silver Group.**

2. If the solution from which $AgCl$, Hg_2Cl_2 and $PbCl_2$ have been removed is first neutralized, then made just acid toward methyl orange test paper, and finally a stream of hydrogen sulfide, H_2S, is passed in, the cations: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++} and Sn^{++++} will be precipitated as sulfides, having the following formulas: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS and SnS_2. The sulfides of the other cations remaining in the solution cannot form in such an acidified solution. This procedure therefore enables us to remove the above-named cations from the remaining ones. This group of cations is known as **Group II,** the **Hydrogen Sulfide Group** or the **Copper-Tin Group.** It should be noted that lead is included here as well as in Group I, since the detection of lead in Group I may fail.

3. If now the solution which remains is treated with a small quantity of NH_4Cl to prevent the precipitation of $Mg(OH)_2$ and an excess of NH_4OH added, the hydroxides of iron, manganese, aluminum and chromium are precipitated as $Fe(OH)_3$, $Mn(OH)_2$, $Al(OH)_3$ and $Cr(OH)_3$ and nickel, cobalt and zinc are transformed into complex metal-ammonia ions. After removal of the hydroxides, the passage of a stream of H_2S into the solution will precipitate NiS, CoS and ZnS. The four hydroxides are designated as **Group III, Subdivision A,** and the sulfides as **Group III, Subdivision B.** The group as a whole will hereafter be referred to as the **Ammonium Hydroxide** and **Ammonium Sulfide Group.**

4. Finally, if to the remaining filtrate we add a solution of ammonium carbonate, $(NH_4)_2CO_3$, the carbonates of barium, strontium and calcium form. These constitute **Group IV,** the **Ammonium Carbonate** or **Alkaline Earth Group.**

5. Magnesium, potassium, sodium and the ammonium ion remain. There is no group precipitating agent for these, and they are tested for separately. This is **Group V,** the **Soluble Cation Group.**

GROUP I. THE HYDROCHLORIC ACID GROUP

SILVER, Ag^+
MERCUROUS MERCURY, Hg_2^{++}
LEAD, Pb^{++}

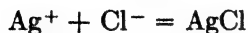
Silver chloride, AgCl, and mercurous chloride, Hg_2Cl_2, are very insoluble in cold and hot water and in acids such as dilute HCl. Lead chloride, $PbCl_2$, is appreciably soluble in cold water and completely so in hot water. In the macro scheme of analysis, upon which this micro scheme is based, the separation of these cations from others is made by the use of dilute HCl, by which action AgCl, Hg_2Cl_2 and usually $PbCl_2$ are precipitated. Silver and mercurous mercury properly constitute Group I, and lead is included only when the amount of lead in the sample is relatively large. Lead chloride dissolves in water to the extent of 11 grams per liter or 0.011 gram per cubic centimeter. This means that if less than 0.9 mg. of lead per cc. is present, $PbCl_2$ will not precipitate. Inasmuch as the test solutions used in the experiments outlined below contain 1 mg. of lead per cc., and since the scheme of systematic analysis provides for samples in which the amount of any metallic constituent may be much less than this amount, $PbCl_2$ will not precipitate in appreciable amounts and may even not precipitate at all.

Group Precipitation and Separation

Experiment 1.—In separate centrifuge tubes place a few drops of Ag^+, and of Hg_2^{++} test solutions. In a third tube dissolve a large crystal of $Pb(NO_3)_2$. Add two drops of dilute HCl to each tube, and note that a white precipitate is formed in each. Place the tubes successively in the hand centrifuge and centrifuge each by a few turns of the handle. Pipet off the supernatant liquid as completely as possible. The ionic precipitating reactions taking place are shown by the equations:

$$Ag^+ + Cl^- = \underline{AgCl}$$

$$Hg_2^{++} + 2Cl^- = \underline{Hg_2Cl_2}$$

$$Pb^{++} + 2Cl^- = \underline{PbCl_2}$$

Experiment 2.—To the tubes containing the respective chlorides add five drops of water and heat carefully to boiling over the micro burner. It will be noted that AgCl and Hg_2Cl_2 do not dis-

solve, but that $PbCl_2$ dissolves completely, in hot water. This behavior of $PbCl_2$ furnishes the means of separating silver and mercurous mercury, in the form of their chlorides, from lead. Reserve the tubes with their contents for the next experiment.

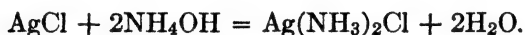
Experiment 3.—To the tubes containing AgCl and Hg_2Cl_2 add a few drops of NH_4OH. Note that the silver chloride dissolves and the mercurous chloride is converted into a black residue. The behavior of these chlorides toward NH_4OH, to be explained later, is utilized in the systematic analysis to separate silver from mercurous mercury.

Properties and Tests

SILVER, Ag^+

Most of the salts of silver are insoluble in water and some are insoluble even in HNO_3. Silver nitrate is soluble in water and finds important uses as a reagent. The properties of AgCl have already been revealed in the group experiments.

The chlorides of silver and of mercurous mercury are alike in their behavior towards acids and hot water, as shown by Experiments 1 and 2. The means of separating them, for the purpose of identification, lies in their action toward NH_4OH, as shown in Experiment 3. The AgCl dissolves in NH_4OH according to the reaction:

$$AgCl + 2NH_4OH = Ag(NH_3)_2Cl + 2H_2O.$$

The complex salt, $Ag(NH_3)_2Cl$, silver-ammonia-chloride, may be considered completely ionized, forming the complex $Ag(NH_3)_2{}^+$ ion. From a solution containing the complex salt, silver chloride can be reprecipitated by neutralizing the ammoniacal solution with dilute nitric acid, the reaction being:

$$Ag(NH_3)_2{}^+ + Cl^- + 2H^+ + 2NO_3{}^- = \underline{AgCl} + 2NH_4{}^+ + 2NO_3{}^-.$$

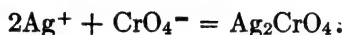
This constitutes one of the simplest tests for silver. The test is best observed by withdrawing a drop of the solution and placing it on a black spot plate or on a glass slide and then adding a drop of dilute HNO_3.

Hydrogen sulfide precipitates black Ag_2S. Since H_2S is the precipitating agent for Group II, it is important in a systematic analysis to remove the silver as completely as possible as AgCl in Group I. The sulfide is soluble in HNO_3.

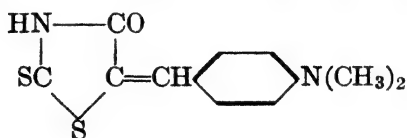
Tests for Silver

The precipitation of AgCl by adding HNO_3 to a solution of the complex silver-ammonia ion is, as already indicated, a test for silver but not a very sensitive one. Two more sensitive tests are here described and several others referred to.

Potassium Chromate Test.—Silver salt solutions react with soluble chromates to produce a red precipitate of silver chromate according to the reaction:

$$2Ag^+ + CrO_4^{=} = \underline{Ag_2CrO_4}.$$

To conduct this reaction as a microchemical test, proceed as follows: Place a drop of the test solution on the spot plate and add a drop of $(NH_4)_2CO_3$ solution. Remove the clear liquid from the precipitate and add to it a drop of K_2CrO_4 solution containing acetic acid. The characteristic red color of Ag_2CrO_4 appears. The test may also be performed, as recommended by Feigl,[1] by the use of filter paper or drop-reaction paper, when the silver chromate will appear as a red ring.

Dimethyl-Amino-Benzylidine-Rhodanine Test.—This test was first proposed by Feigl.[2] The compound has the formula,

```
HN——CO
 |    |
SC    C=CH<  >N(CH3)2
  \  /
   S
```

To a drop of silver nitrate test solution on a spot plate or on drop-reaction paper add a drop of the reagent and note the formation of a red or reddish-violet coloration. The test is made more sensitive by slightly acidifying the test drop with dilute nitric acid.

The reagent also reacts with mercury, lead and copper salts, but it may be used according to the modification introduced by Heller and Krumholz[3] as a specific test for silver by first adding a 5 per cent solution of KCN to the test solution and acidifying with dilute nitric acid. Gold, platinum and palladium also respond to this reagent.[4,5]

A further modification of this test has been proposed by G. Ettisch and J. Tamchyna,[6] by which a suitably prepared collodion membrane is impregnated with the silver solution and the reagent, thus making the test extremely delicate.

Additional Tests for Silver

A number of other tests have been proposed among which the following may be mentioned, the details of which must be sought in the references given: The oxidation of manganese to permanganate catalyzed by means of a silver salt has been made the basis of a sensitive test for silver by Denigès.[7] Another catalytic reaction, using sodium hypophosphite to reduce mercurous chloride, is found to be accelerated by the presence of silver, and this has been proposed by Hahn [8] as a test for silver. H. Fischer's [9] method, using diphenyl thiocarbazone (dithizone), reacts with silver but also with a large number of other cations. Manganese nitrate in the presence of NaOH,[10] and stannous chloride[11] are still other tests recently recommended.

[1] F. Feigl, Tüpfelreaktionen, 2nd Ed., 142.

[2] F. Feigl, Z. anal. Chem. **74**, 380 (1928); C. A. 4080 (1928).

[3] K. Heller and P. Krumholz, Mikrochemie **7**, 213 (1929); C. A. 1818 (1930).

[4] H. Holzer, Mikrochemie [N. S.] **2**, 271 (1930); C. A. 1757 (1931).

[5] F. Feigl, P. Krumholz and E. Rajmann, Mikrochemie **3**, **165** (1931); C. A. 2387 (1931).

[6] G. Ettisch and J. Tamchyna, Mikrochemie [2] **4**, 92 (1931); C. A. 45 (1932).

[7] G. Denigès, Bull. soc. chim. **51**, 1096 (1932); C. A. 44 (1933). Bull. soc. pharm. Bordeaux **70**, 13 (1932); C. A. 3393 (1933).

[8] F. Hahn, Ber. **65B**, 840 (1932); C. A. 4007 (1932).

[9] H. Fischer, Z. angew. Chem. **42**, 1025 (1929); C. A. 567 (1930). Mikrochemie **2**, 319 (1930); C. A. 893 (1931).

[10] N. A. Tananaev and Iv. Tananaev, Z. anorg. allgem. Chem. **170**, 113 (1928); C. A. 1930 (1928).

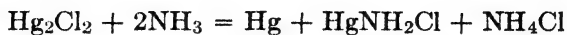
[11] N. A. Tananaev, Z. anorg. allgem. Chem. **140**, 320 (1924); C. A. 1108 (1925).

MERCUROUS MERCURY, Hg_2^{++}

The element mercury forms two series of salts, the mercurous and the mercuric, the valence in the former being 1 and in the latter 2. The mercurous ion, however, is a double atom having two charges and is written Hg_2^{++}; the mercuric ion is written Hg^{++}. The mercurous ion, as shown in Experiment 1, is precipitated by the chloride ion, forming Hg_2Cl_2, a white salt insoluble in HCl. This fact places this form of mercury in Group I; the mercuric ion is a member of Group II.

Mercurous chloride, like AgCl, is insoluble in hot water (see

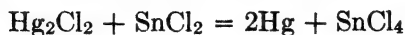
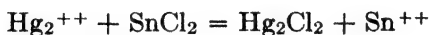
Experiment 2). With NH_4OH, as revealed in Experiment 3, a reaction takes place, forming a mixture of black, finely divided metallic mercury and white, insoluble mercuric amido chloride, $HgNH_2Cl$. The reaction may be most simply expressed by the equation:

$$Hg_2Cl_2 + 2NH_3 = \underline{Hg} + \underline{HgNH_2Cl} + NH_4Cl$$

This property not only serves to separate mercurous chloride from silver chloride, but also, by the formation of the black precipitate, furnishes evidence of the presence of the mercurous ion. Ordinarily, in a systematic analysis, the further identification of the presence of mercury in this group is made by dissolving the black mixture in an oxidizing solvent such as $KClO_3$ acidified with HCl thus oxidizing it to the mercuric state and then by applying tests for the mercuric ion. Nevertheless, though the final confirmation of mercury rests upon reactions of the mercuric ion, several specific tests have been proposed for the mercurous ion, and these tests, described in the following paragraphs, may be tried, using a solution of mercurous nitrate as the test substance.

Tests for the Mercurous Ion

Stannous Chloride Test.—To a drop of Hg_2^{++} test solution placed on a glass slide or on a black spot plate add two drops of $SnCl_2$ solution. An immediate white precipitate of Hg_2Cl_2 forms, which quickly turns gray, then black, owing to the formation of metallic mercury.

$$Hg_2^{++} + SnCl_2 = \underline{Hg_2Cl_2} + Sn^{++}$$

$$Hg_2Cl_2 + SnCl_2 = \underline{2Hg} + SnCl_4$$

Gallic Acid Test.—A freshly prepared alcoholic solution of gallic acid is found to react with a mercurous salt solution to give an orange color. In dilute solution the color shades into yellow. No cations of Groups I and II interfere with this reaction.

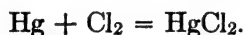
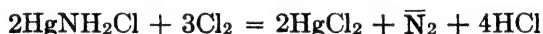
Potassium Nitrite Test.—A drop of a concentrated solution of KNO_2 added to a drop of Hg_2^{++} test solution on drop-reaction paper will give a black spot, as the result of the formation of metallic mercury by reduction. This test is specific. Colored ions give a brown coloration, which may be washed off, revealing the black spot.[1]

Tests for the Mercuric Ion

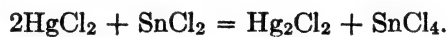
Either mercuric nitrate test solution may be used for the tests outlined below or else the precipitate obtained in Experiment 3 may be dissolved by the following procedure:

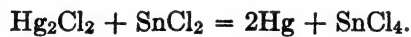
Centrifuge the black mixture of mercury and mercuric amido chloride obtained in Experiment 3 by the action of ammonia on mercurous chloride and pipet off and discard the supernatant liquid. Add a crystal of $KClO_3$ and a drop of concentrated HCl. Warm the tube carefully until the mass is dissolved, and then boil vigorously to remove excess chlorine. The chlorine produced by the action of concentrated HCl on $KClO_3$ may be considered the active solvent, the reaction being represented by the equations:

$$2HgNH_2Cl + 3Cl_2 = 2HgCl_2 + \overline{N}_2 + 4HCl$$

$$Hg + Cl_2 = HgCl_2.$$

Boil the solution until free chlorine is no longer evolved.

Stannous Chloride Test for Mercuric Ion.—To a drop of the mercuric solution, placed on a glass slide, add a drop of stannous chloride reagent. A white precipitate of Hg_2Cl_2 first forms by the reducing action of $SnCl_2$:

$$2HgCl_2 + SnCl_2 = \underline{Hg_2Cl_2} + SnCl_4.$$

Further reduction to metallic mercury takes place, causing the precipitate to become gray and finally black:

$$Hg_2Cl_2 + SnCl_2 = \underline{2Hg} + SnCl_4.$$

Tananaev [2] has developed this reaction as a stain test by mixing a drop of the mercuric solution with a drop of aniline and adding this mixture to a drop of stannous chloride on drop-reaction paper, a black stain appearing immediately.

Diphenyl-Carbazide Test.—Place a drop of the carbazide reagent on drop-reaction paper or on the spot plate; add a drop of Na_2CO_3 solution and then a drop of mercuric test solution. This reagent was adapted as a micro test by Feigl and Neuber.[3, 4, 5] It has the formula $OC = (NH - NHC_6H_5)_2$ and yields with mercury a blue color.

Double Thiocyanate Test.—Place a drop of Hg^{++} test solution on the spot plate; add a crystal of NH_4CNS and then a little solid cobalt acetate. A blue color, due to the formation of the double salt $Co(CNS)_2 \cdot Hg(CNS)_2$, is produced. See in this connection the papers by Ormont[6] and by de Sweemer.[7]

Other Tests for Mercury

Dimethyl - Amino - Benzylidine - Rhodanine Reaction.—This reagent, recommended as a test for silver, may also be used under special conditions as a test for mercury, as suggested by Heller and Krumholz.[8] A drop of the reagent is placed on a spot plate and a drop of neutral test solution added. A red color appears. This test cannot be used in the presence of silver. Acids interfere but may be overcome by adding several drops of a saturated sodium acetate solution. By adding several drops of a concentrated Na_2HPO_4 solution the test may be used to detect mercury in the presence of copper.

Among other microchemical tests recently proposed for mercury, the following may be mentioned. The reaction of mercuric ion with KI which has been sensitized by Denigès,[9] who uses $HgI_2 \cdot 2KI$ as a reagent instead of KI alone, HgI_2 forming a red precipitate on the spot plate. The cuprous mercuric iodide test suggested by Artmann;[10] this is brought about by coating reaction paper with cuprous iodide and adding a drop of the mercuric solution, a bright red color, due to cuprous mercuric iodide, resulting. Denigès [11] also recommends zinc purpurate, which gives a pink color, though the test is not very sensitive.

[1] N. A. Tananaev, Ukrain. Khem. Zhur., Sci. Pt. **5**, 63 (1930); see also Mikrochemie **9**, 185 (1931); C. A. 5669 (1930).

[2] N. A. Tananaev, Z. anorg. allgem. Chem. **133**, 372 (1924); C. A. 1628 (1924). Z. anorg. allgem. Chem. **140**, 320 (1924); C. A. 1108 (1925).

[3] F. Feigl and F. Neuber, Z. anal. Chem. **62**, 370 (1923); C. A. 2687 (1923).

[4] I. Kolthoff, Chem. Weekblad **21**, 20 (1924); C. A. 1797 (1924).

[5] A. Scott, J. Am. Chem. Soc. **51**, 3351 (1929); C. A. 566 (1930).

[6] B. Ormont, Z. anal. Chem. **70**, 308 (1927); C. A. 1779 (1927).

[7] A. de Sweemer, Mikrochemie **12**, 223 (1932); C. A. 678 (1933).

[8] K. Heller and P. Krumholz, Mikrochemie **7**, 213 (1929); C. A. 1818 (1930).

[9] G. Denigès, Bull. soc. pharm. Bordeaux **68**, 207 (1930); C. A. 4769 (1932).

[10] P. Artmann, Z. anal. Chem. **60**, 81 (1921); C. A. 2808 (1921).

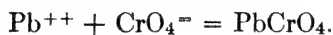
[11] G. Denigès, Ann. chim. anal. **3**, 251 (1921); C. A. 3043 (1922).

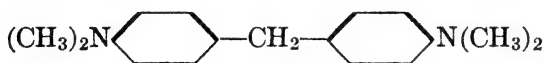
LEAD, Pb^{++}

Lead chloride is appreciably soluble in cold water and much more so in hot water. Whether lead will precipitate as $PbCl_2$ from a mixture of metallic ions upon the addition of HCl and thus be included as a member of Group I depends upon the amount of lead ion present. Lead ions are, however, easily precipitated by hydrogen sulfide and are included in Group II where provision is there made for the further detection of lead should it fail to be detected in Group I.

Tests for Lead

K_2CrO_4 Test.—To a few drops of Pb^{++} test solution, or to a drop of the contents of the tube from Experiment 2, add a drop of K_2CrO_4 reagent. The yellow precipitate is $PbCrO_4$, and the simple ionic reaction is:

$$Pb^{++} + CrO_4^{=} = \underline{PbCrO_4}.$$

Tetra-Methyl-Diamino-Diphenyl-Methane Test.[1]—Place a drop of 3 per cent H_2O_2 on drop-reaction paper; add a drop of dilute NH_4OH and immediately a drop of Pb^{++} test solution. Allow to stand for several minutes to decompose the excess H_2O_2, and then add a drop of the reagent. A blue color appears. This is not a specific test for lead. This organic compound has the formula:

$$(CH_3)_2N\langle\quad\rangle{-}CH_2{-}\langle\quad\rangle N(CH_3)_2$$

The composition of the blue oxidation product has not yet been determined. Benzidine, $H_2N{-}\langle\quad\rangle{-}\langle\quad\rangle{-}NH_2$, may be used in place of the tetra methyl base, as recommended by Feigl and Neuber,[1] by Denigès [2] and by Tougarinoff,[3] the oxidation product being blue.

Additional Tests for Lead

Resorcinol Test.—Place a drop of the lead solution on spot paper; add a drop of dilute NH_4OH and then a drop of 5 per cent aqueous solution of resorcinol.[4] A blue color forms in the course of several minutes. A brown color may form at first, but is not to be taken as the test.

Carminic Acid Test.—Carminic acid, first proposed by Pavelka [5] as a test reagent for lead, gives a distinctive bluish-violet color when the test is conducted according to the following procedure. Two drops of the reagent are placed on drop-reaction paper and allowed to dry. Then a drop of lead solution is added to one of the spots, leaving the other as a blank, and both are developed over concentrated NH_4OH. After drying, a definitely violet-blue colored spot remains. The interference of the color of the reagent may be lessened by adding a few drops of water to the spot after the NH_3 development, so that the colored solution is removed by capillarity from the precipitate.

The same investigator has also studied the reaction of lead with gallocyanin and pyridine, carried out on filter paper, by first placing a drop of the lead solution on a strip of paper, adding a drop of dilute pyridine followed by a 0.1 per cent solution of gallocyanin, the spot after washing successively with dilute pyridine becoming violet in color.

Dithizone is recommended as a test for lead by Fischer.[6] Tananaev[7,8] suggests $SnCl_2$ and KI; the nitroso derivative of R-salt is proposed by Bernardi and Schwartz.[9] Tamchyna [10] notes that viscose in a dilute neutral or slightly acid solution gives a red color with lead; certain other ions also give colored products with this reagent.

[1] F. Feigl and F. Neuber, Z. anal. Chem. **62**, 371 (1923); C. A. 2687 (1923).
[2] G. Denigès, Précis de chimie anal. 4 ed. 72 (1913).
[3] B. Tougarinoff, Ann. soc. sci. Bruxelles **50**, 145 (1930); C. A. 1456 (1931).
[4] L. Bey and M. Faillebin, Bull. soc. chim. **47**, 225 (1930); C. A. 2397 (1930).
[5] F. Pavelka, Mikrochemie **7**, 301 (1929); C. A. 3965 (1930).
[6] H. Fischer, Mikrochemie [N. S.] **2**, 319 (1930); C. A. 893 (1931).
[7] N. Tananaev, Z. anorg. allgem. Chem. **167**, 81 (1927); C. A. 367 (1928).
[8] N. Tananaev and I. Tananaev, Z. anorg. allgem. Chem. **167**, 341 (1927); C. A. 736 (1928).
[9] A. Bernardi and M. Schwartz, Ann. chim. applicata **21**, 45 (1931); C. A. 2937 (1931).
[10] J. Tamchyna, Chem. Listy **24**, 31 (1930); C. A. 2395 (1930).

EXERCISE. PRACTICE ANALYSIS OF A MIXTURE OF SILVER, LEAD AND MERCUROUS MERCURY. Prepare a mixture by taking from the stock test solution bottles one drop of Ag^+ ion solution, one drop of Hg_2^{++} ion solution and five drops of Pb^{++} ion solution. This mixture will contain approximately 1 mg. of Ag^+,

1 mg. of Hg_2^{++} and 5 mg. of Pb^{++}. Place the mixture in a centrifuge tube and add a few drops of dilute HCl. Centrifuge the solution and, to make certain that the chlorides are precipitated as completely as possible, add one more drop of HCl. If a precipitate forms, add several drops and again centrifuge. Pipet off and discard the supernatant liquid.

Add enough water to make the volume about 1 cc. and heat to boiling. The hot water will dissolve the $PbCl_2$ but not the AgCl nor the Hg_2Cl_2. Pipet off the solution and reserve it for tests for lead.

Treat the two chlorides remaining in the tube with dilute NH_4OH. The AgCl will dissolve, being transformed into $Ag(NH_3)_2^+$ ions. The mercurous chloride will be changed into a black residue containing metallic mercury and mercuric amido chloride. Pipet off the solution and dissolve the residue by adding a few crystals of $KClO_3$ and a few drops of concentrated HCl.

These processes have effected the separation of the three cations constituting this group. The steps are shown diagrammatically in the following scheme:

Mixture Containing:		*Precipitate*:		*Residue*:		*Solution*:
Ag^+	Treated with dilute HCl; centrifuged filtrate discarded	AgCl	Treated with hot water	AgCl	NH_4OH	$Ag(NH_3)_2^+$
Hg_2^{++}		Hg_2Cl_2		Hg_2Cl_2		*Residue*:
Pb^{++}		$PbCl_2$		*Solution*: Pb^{++}		$HgNH_2Cl + Hg$

Identification of the Ions of this Group. *Lead.*—The lead, as Pb^{++} ions, is now in the filtrate from the hot water treatment. This solution on cooling may deposit fine needles of $PbCl_2$. Individual drop portions of this solution should now be tested for lead, utilizing for this purpose the tests described under the properties and reactions of lead.

Mercury.—The black residue is the first indication of the presence of mercury. When this is dissolved in $KClO_3$ and concentrated HCl, the solution contains the mercury in the form of mercuric ions. The solution should be boiled to remove free chlorine and separate portions tested by the reagents suggested as tests for mercuric mercury.

Silver.—The solution pipetted from the centrifuge tube after the NH_4OH treatment contains the silver in the form of $Ag(NH_3)_2^+$

ions. A drop of this should be removed, placed on a glass slide or black spot plate and acidified with dilute HNO_3. The white precipitate of AgCl shows the presence of silver. Other portions of the ammoniacal solution should also be used for confirmatory tests for silver, and record made of the results.

GROUP II. THE HYDROGEN SULFIDE GROUP

MERCURIC MERCURY, Hg^{++}
LEAD, Pb^{++}
BISMUTH, Bi^{+++}
COPPER, Cu^{++}
CADMIUM, Cd^{++}
ARSENIC, As^{+++} and As^{+++++}
ANTIMONY, Sb^{+++} and Sb^{+++++}
TIN, Sn^{++} and Sn^{++++}

This group is characterized by the insolubility of its sulfides in dilute hydrochloric acid. The precipitating agent is H_2S, which precipitates these ions as sulfides in a solution somewhat acidic under conditions which prohibit other sulfides from forming.

Group Precipitation and Subdivision

Experiment 4.—Using a few drops of test solution (in the cases of arsenic, antimony and tin it is sufficient for this experiment to employ only those in the lower state of oxidation) in separate centrifuge or test tubes, add a drop of dilute HCl and pass H_2S into each tube until a precipitate forms. A few drops of a freshly prepared solution of H_2S may conveniently be used in this experiment to carry out the precipitation. The essential ionic reactions taking place, including both forms of the three last named elements, are:

$$Hg^{++} + S^{=} = \underline{HgS} \text{ (black)}$$

$$Pb^{++} + S^{=} = \underline{PbS} \text{ (black)}$$

$$2Bi^{+++} + 3S^{=} = \underline{Bi_2S_3} \text{ (brownish-black)}$$

$$Cu^{++} + S^{=} = \underline{CuS} \text{ (black)}$$

$$Cd^{++} + S^{=} = \underline{CdS} \text{ (yellow)}$$

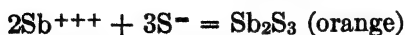
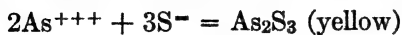
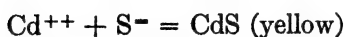
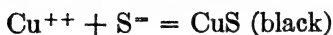
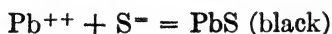
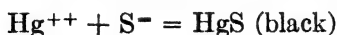
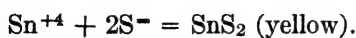
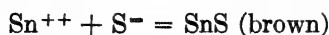
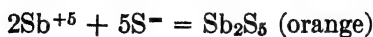
$$2As^{+++} + 3S^{=} = \underline{As_2S_3} \text{ (yellow)}$$

$$2As^{+5} + 5S^{=} = \underline{As_2S_5} \text{ (yellow)}$$

$$2Sb^{+++} + 3S^{=} = \underline{Sb_2S_3} \text{ (orange)}$$

$$2Sb^{+5} + 5S^{=} = \underline{Sb_2S_5} \text{ (orange)}$$

$$Sn^{++} + S^{=} = \underline{SnS} \text{ (brown)}$$

$$Sn^{+4} + 2S^{=} = \underline{SnS_2} \text{ (yellow).}$$

The sulfides of this group are separated into two divisions or subgroups by the action of sodium polysulfide, Na_2S_2. The following experiment will show the action of this reagent on the individual sulfides.

Experiment 5.—Centrifuge, pipet off the solution and then add to each precipitate three drops of Na_2S_2 solution. Heat gently, meanwhile stirring the mixture with a platinum wire. The sulfides of arsenic, antimony and tin dissolve (a small amount of yellow residue consisting of sulfur may be left in some cases) with the formation of complex metal-thio ions. Mercuric sulfide may also dissolve to a small extent in this reagent. The reactions are shown by the following equations:

$$As_2S_3 + 3Na_2S_2 = 2Na_3AsS_4 + \underline{S}$$

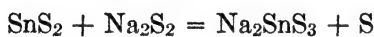
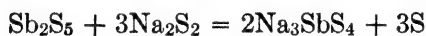
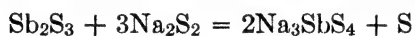
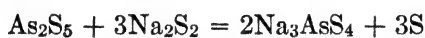
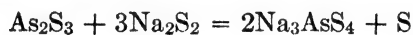
$$As_2S_5 + 3Na_2S_2 = 2Na_3AsS_4 + \underline{3S}$$

$$Sb_2S_3 + 3Na_2S_2 = 2Na_3SbS_4 + \underline{S}$$

$$Sb_2S_5 + 3Na_2S_2 = 2Na_3SbS_4 + \underline{3S}$$

$$SnS + Na_2S_2 = Na_2SnS_3$$

$$SnS_2 + Na_2S_2 = Na_2SnS_3 + \underline{S}$$

$$HgS + Na_2S_2 = Na_2HgS_2 + \underline{S}.$$

The action of Na_2S_2 thus provides a means of separating this group into two divisions, designated as Division A and containing HgS, PbS, Bi_2S_3, CuS and CdS, and as Division B containing the arsenic, antimony and tin and possibly small amounts of mercury in the form of complex thio ions.

Separation of the Ions of Division A, Group II

Experiment 6. Action of Dilute HNO_3 on the Sulfides of this Subgroup.—Add a few drops of dilute HNO_3 to the tubes containing HgS, PbS, Bi_2S_3, CuS and CdS. Warm the tubes. Dis-

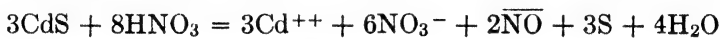
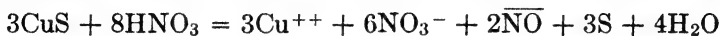
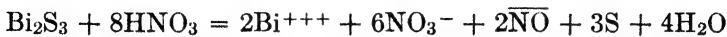
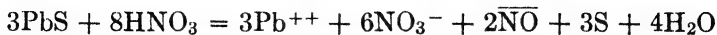
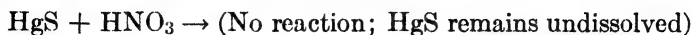
solving of the sulfides takes place except in the case of HgS, as shown by the following equations:

$$\underline{HgS} + HNO_3 \rightarrow \text{(No reaction; HgS remains undissolved)}$$

$$\underline{3PbS} + 8HNO_3 = 3Pb^{++} + 6NO_3^- + 2\overline{NO} + \underline{3S} + 4H_2O$$

$$\underline{Bi_2S_3} + 8HNO_3 = 2Bi^{+++} + 6NO_3^- + 2\overline{NO} + \underline{3S} + 4H_2O$$

$$\underline{3CuS} + 8HNO_3 = 3Cu^{++} + 6NO_3^- + 2\overline{NO} + \underline{3S} + 4H_2O$$

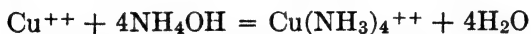
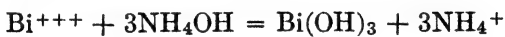
$$\underline{3CdS} + 8HNO_3 = 3Cd^{++} + 6NO_3^- + 2\overline{NO} + \underline{3S} + 4H_2O$$

The insolubility of HgS in nitric acid makes it possible to separate it from the sulfides of the other members of this sub-group.

Experiment 7. Separation of Lead as $PbSO_4$.—Add dilute H_2SO_4 to test solutions containing Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++}. Note the formation of a precipitate of $PbSO_4$ only in the case of lead. This property enables one to separate lead from bismuth, copper and cadmium.

Experiment 8. Separation of Bismuth as $Bi(OH)_3$.—To test solutions containing Bi^{+++}, Cu^{++} and Cd^{++} ions add, dropwise, an excess of dilute NH_4OH. The white precipitate formed in the bismuth solution remains insoluble in an excess of the reagent whereas the copper hydroxide redissolves to form a deep blue solution and the $Cd(OH)_2$ redissolves to form a clear colorless solution. The reactions are:

$$Bi^{+++} + 3NH_4OH = \underline{Bi(OH)_3} + 3NH_4^+$$

$$Cu^{++} + 4NH_4OH = Cu(NH_3)_4^{++} + 4H_2O$$

$$Cd^{++} + 4NH_4OH = Cd(NH_3)_4^{++} + 4H_2O.$$

The further separation of copper from cadmium for the purpose of applying tests for cadmium is discussed under cadmium.

Properties and Tests, Group IIA

MERCURIC MERCURY, Hg^{++}

Attention has already been called to the fact that mercuric ion is not precipitated by the chloride ion, thus excluding this form of mercury from Group I and placing it in Group II along

with the other ions which are precipitated as sulfides with H_2S in a slightly acidic solution.

The group experiments with individual solutions of ions of this group have shown, in regard to divalent mercury, that the sulfide is readily precipitated by H_2S, that it may to a slight extent dissolve in Na_2S_2 and that it is insoluble in dilute HNO_3.

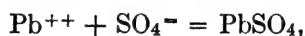
HgS may be dissolved in $KClO_3$ and concentrated HCl, in aqua regia or in bromine water.

The tests for the mercuric ion have already been described in connection with Group I.

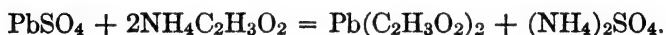
LEAD, Pb^{++}

The failure of lead to precipitate completely as $PbCl_2$ in Group I and the certainty of incomplete removal of $PbCl_2$ necessitate the inclusion of lead in Group II. The group experiments have shown that the sulfide is precipitated by H_2S, and that this is insoluble in polysulfides such as Na_2S_2. PbS is soluble in dilute HNO_3 as shown in Experiment 6.

The separation of lead from bismuth, copper and cadmium has been shown, in Experiment 7, to consist of the precipitation of lead sulfate:

$$Pb^{++} + SO_4^{=} = \underline{PbSO_4},$$

the sulfates of the other three elements being very soluble.

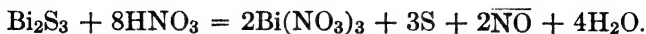
Lead sulfate is very insoluble in water and in the usual acid solvents. It does, however, dissolve in ammonium acetate, forming non-ionized lead acetate:

$$PbSO_4 + 2NH_4C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4.$$

Tests for lead have already been given in connection with the discussion of lead in Group I.

BISMUTH, Bi^{+++}

Bismuth ordinarily has the valence of +3, though sometimes a valence of 5 is shown as, for instance, in the bismuthates such as $NaBiO_3$. Solutions containing bismuth salts are readily hydrolyzed; thus, if a solution of $BiCl_3$ or $Bi(NO_3)_3$ is considerably diluted with water, the basic salt, bismuth oxychloride, BiOCl, or the oxynitrate, $BiONO_3$, will be precipitated. The addition of HCl or HNO_3 will dissolve the basic salt.

The sulfide, Bi_2S_3, as shown in Experiment 4, is readily precipitated by H_2S, even in the presence of HCl. The sulfide is soluble in dilute HNO_3, the reaction taking place according to the equation:

$$Bi_2S_3 + 8HNO_3 = 2Bi(NO_3)_3 + \underline{3S} + 2\overline{NO} + 4H_2O.$$

Bismuth sulfate is soluble in water and does not precipitate when sulfuric acid is added to a solution containing bismuth ions (distinction from lead); a basic sulfate may, however, form on fuming down the solution.

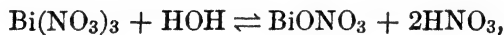
The hydroxide, $Bi(OH)_3$, a white insoluble compound, is precipitated when NH_4OH is added to a solution containing bismuth ions, as shown in Experiment 8. The precipitate is insoluble in an excess of NH_4OH, in which respect it differs from the hydroxides of copper and cadmium, and this offers the means of separating this ion from the latter two ions.

Tests for Bismuth

Hydrolysis of $Bi(NO_3)_3$.—To a drop of Bi^{+++} test solution on a glass slide or black spot plate add water, drop by drop, until a white precipitate is obtained. This is a basic nitrate, formed by hydrolysis:

$$Bi(NO_3)_3 + HOH \rightleftharpoons \underline{BiONO_3} + 2HNO_3,$$

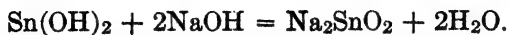
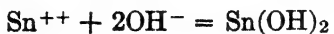
or written ionically:

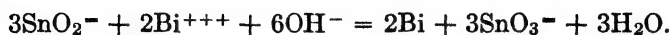
$$Bi^{+++} + 3NO_3^- + H_2O \rightleftharpoons \underline{BiONO_3} + 2H^+ + 2NO_3^-.$$

The oxychloride, BiOCl, is formed when a $BiCl_3$ solution is diluted with water.

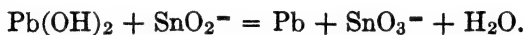
This behavior is sometimes utilized as a test for bismuth, though the test is not very sensitive. More sensitive tests are described below.

Sodium Stannite Test.[1]—On the spot plate prepare sodium stannite by adding dilute NaOH to several drops of stannous chloride solution until the precipitate which first forms redissolves:

$$Sn^{++} + 2OH^- = \underline{Sn(OH)_2}$$

$$\underline{Sn(OH)_2} + 2NaOH = Na_2SnO_2 + 2H_2O.$$

Place a drop of this solution in a depression of the spot plate and add to it a drop of bismuth test solution. A black precipitate or a brown color forms, due to reduction of the bismuth ion to the metallic state:

$$3SnO_2^{=} + 2Bi^{+++} + 6OH^- = \underline{2Bi} + 3SnO_3^{=} + 3H_2O.$$

Feigl and Krumholz [2] have modified this test by adding a lead salt, the reduction of which by the stannite is catalyzed by the presence of the bismuth ion. If a drop of an acidified bismuth solution and one of a saturated $PbCl_2$ solution are mixed with two drops of the stannite solution, a black precipitate forms immediately or a brown color appears in a short time, depending upon the quantity of bismuth added.

$$Pb(OH)_2 + SnO_2^{=} = \underline{Pb} + SnO_3^{=} + H_2O.$$

Since a color will appear in a few minutes even in the absence of bismuth, a blank test must always be run. A number of other metals, such as Ag, Hg and Cu, interfere with this test.

Cinchonine-Potassium Iodide Test.[3]—To a drop of bismuth test solution on a spot plate add a drop of cinchonine-KI reagent. A red precipitate forms, due to the formation of a double salt of the type $BiI_3 \cdot$cinchonine$\cdot HI$. The test solution should be only slightly acidic. Increase in the acid concentration lowers the sensitivity of the test until finally no reaction is obtained. This test is known as Léger's test.

This reaction is not peculiar to cinchonine since brucine and other alkaloids [4] give similar reactions. In this connection it is interesting to note that bismuth salts are commonly used as reagents for detecting and identifying alkaloids. Cinchonine is an alkaloid derived from quinoline. Other quinoline derivatives such as α-and β-naphthoquinoline and 8-hydroxyquinoline [5,6] have been suggested as tests for bismuth.

Additional Reactions of Bismuth

Cesium Chloride-Potassium Iodide Test.[6]—Place a drop of test solution on a spot plate. Add a small crystal of KI and then one of cesium chloride, CsCl. A blood-red precipitate, which has the formula $2CsI \cdot BiI_3 \cdot 5H_2O$, is formed. Potassium iodide alone may be used to give a test in the following manner.[7] Place a drop

of 5 per cent KI solution on spot paper and add a drop of bismuth test solution. A brownish-black precipitate of BiI_3 forms, dissolving in excess KI solution to give a yellow or orange solution containing the complex BiI_4^- ion. Mercury interferes with this test by forming orange HgI_2.

Among other tests that have been proposed the following may be mentioned:

Dimethylglyoxime,[8] $(CH_3C)_2(NOH)_2$, added to a hot solution of $BiCl_3$ or $Bi(NO_3)_3$ and made strongly alkaline with NH_4OH, gives a yellow precipitate. If $Bi_2(SO_4)_3$ is used a white precipitate is obtained. This test is especially recommended by Tougarinoff.[9] Ammonium tetra-cetyl[10] added to a drop of test solution on drop-reaction paper gives a red coloration. Cobalt ethylenediamine chloride,[11] $[Co(CH_2NH_2CH_2NH_2)_3]Cl_3 \cdot 3H_2O$, in the presence of excess KI solution (which forms $KBiI_4$), gives a reddish-yellow precipitate of $[BiI_4]_2[Co(CH_2NH_2CH_2NH_2)_2]I$. This reaction has been used for the gravimetric determination of bismuth. Thiourea,[12] $NH_2 \cdot CS \cdot NH_2$, gives with Bi^{+++} ion a yellow color which changes to orange when the solution is made alkaline and heated, and finally deposits a black precipitate.

If a drop of bismuth solution is heated on a calcium carbonate button (made by heating a calcium carbonate paste) in a small hydrogen flame, the flame of BiH_3 acquires a cornflower-blue luminescence.[13]

Viscose, as suggested by Tamchyna,[14] in a 0.05 per cent aqueous solution gives with bismuth salts, in neutral or very weakly acidic solutions a red-brown precipitate.

[1] L. Vanino and F. Treubert, Ber. **31**, 1113 (1898).

[2] F. Feigl and P. Krumholz, Ber. **62B**, 1138 (1929); C. A. 4160 (1929).

[3] F. Feigl and F. Neuber, Z. anal. Chem. **62**, 369 (1923); C. A. 2687 (1923).

[4] R. Berg and O. Wurm, Ber. **60B**, 1664 (1927); C. A. 3581 (1927).

[5] R. Sazerac and J. Pouzergues, Compt. rend. soc. biol. **109**, 79 (1932); C. A. 2391 (1932).

[6] J. Vermande, Pharm. Weekblad **55**, 1131 (1918); C. A. 2294 (1918). C. Meloche and P. V. Clark, J. Am. Chem. Soc. **52**, 907 (1930); C. A. 2394 (1930).

[7] G. Lochmann, Z. anal. Chem. **85**, 241 (1931); C. A. 5865 (1931).

[8] H. Kubina and J. Plichta, Z. anal. Chem. **72**, 11 (1927); C. A. 3851 (1927).

[9] B. Tougarinoff, Ann. soc. sci. Bruxelles B **50**, 145 (1930); C. A. 1456 (1931).

[10] A. Girard and E. Fourneau, Compt. rend. **181**, 610 (1926). Bull. soc. chim. **37**, 1669 (1926); C. A. 725 (1926).

[11] G. Spacu and G. Suciu, Z. anal. Chem. **79**, 196 (1929); C. A. 1053 (1930).
[12] G. Sensi and S. Seghezzo, Ann. chim. applicata **19**, 392 (1929); C. A 1053 (1930).
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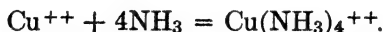
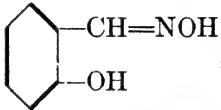
COPPER, Cu^{++}

Copper forms two series of compounds, the cuprous (colorless in solution) in which the copper is monovalent, and the cupric (pale blue in dilute solutions) containing divalent copper. Cuprous compounds are in many ways similar to those of silver and mercurous mercury. Cupric compounds are of more frequent occurrence and of greater importance than cuprous compounds, and for these reasons only the cupric ion is considered here.

The reaction of cupric ions with H_2S forming black CuS, the relative insolubility of CuS in sodium polysulfide and its solubility in HNO_3 have already been considered in the preliminary experiments. With NH_4OH the deep blue complex cupric-ammonia ion forms, which in itself is a good test for the presence of copper, provided enough copper is present to color the solution.

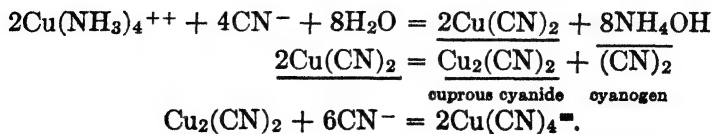
Tests for Copper

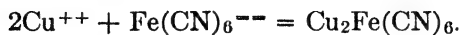
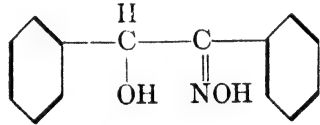
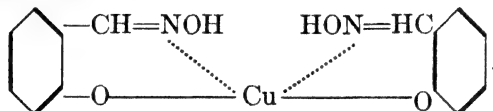
Formation of Complex Ions.—To a drop of copper test solution on a spot plate carefully add a small drop of dilute NH_4OH. A pale blue precipitate of the hydroxide, $Cu(OH)_2$, forms. Now add a few more drops of NH_4OH. The precipitate dissolves with the formation of an intensely blue solution, the color being due to the formation of the complex cupric-ammonia ion:

$$Cu^{++} + 4NH_3 = Cu(NH_3)_4^{++}.$$

If to the blue solution several drops of potassium cyanide solution are added, the color is removed, owing to the formation of the more stable, colorless complex cuprous-cyanide ion, $Cu(CN)_4^{=}$. The following series of reactions takes place:

$$2Cu(NH_3)_4^{++} + 4CN^- + 8H_2O = \underline{2Cu(CN)_2} + 8NH_4OH$$

$$\underline{2Cu(CN)_2} = \underset{\text{cuprous cyanide}}{\underline{Cu_2(CN)_2}} + \underset{\text{cyanogen}}{\overline{(CN)_2}}$$

$$\underline{Cu_2(CN)_2} + 6CN^- = 2Cu(CN)_4^{=}.$$

Ferrocyanide Test.—To a drop of Cu test solution on a spot plate add a drop of dilute HCl and then one of a solution of potassium ferrocyanide, $K_4Fe(CN)_6$. A red precipitate of cupric ferrocyanide results

$$2Cu^{++} + Fe(CN)_6^{----} = \underline{Cu_2Fe(CN)_6}.$$

Salicyl-Aldoxime Test.[1]—Place a drop of test solution on a spot plate and make slightly acid with dilute acetic acid. Then add a drop of salicyl-aldoxime, $C_6H_4(—CH{=}NOH)(—OH)$, solution. A dirty-green precipitate appears, due to the formation of an inner complex salt with the formula

$$C_6H_4\begin{matrix}—CH{=}NOH \\ —O\end{matrix} \cdots Cu \cdots \begin{matrix}HON{=}HC— \\ O—\end{matrix}C_6H_4.$$

This reaction has been used for the gravimetric determination of copper. In place of this reagent, the following one may be employed.

Benzoinoxime (Cupron) Test.[2]—Add a drop of test solution to a drop of a solution of benzoinoxime, $C_6H_5—CH(OH)—C({=}NOH)—C_6H_5$, on spot paper and develop with NH_3. A green color is obtained, the reaction being similar to that with salicyl-aldoxime. However, this test is neither as sensitive nor as specific as that with salicyl-aldoxime.

Many other oximes, such as formaldoxime,[3] α-furil-dioxime and a large number studied by Ephraim[4] give similar reactions.

Additional Tests for Copper

So many tests for copper have been proposed that it is impossible and unecessary even to mention all of them here. Most of these tests involve the use of organic reagents, showing the remarkable variety of compounds with which copper gives a reaction. It is important to remember that, because of this great variety of

reactions, copper interferes with many, if not most, of the tests for the other metals which involve the use of organic compounds. Some of these tests and interferences are mentioned below. For complete information the original references should be consulted.

Double Thiocyanate Test.[5]—If to a drop of test solution on a spot plate a drop of ammonium thiocyanate-mercuric thiocyanate, $2NH_4CNS \cdot Hg(CNS)_2$, solution is added, a green precipitate of $Cu(CNS)_2 \cdot Hg(CNS)_2 \cdot H_2O$ is formed. If this test is carried out in the presence of zinc a violet color is produced (see the double thiocyanate test for zinc); this property may be used to detect either copper or zinc.

Dimethylglyoxime[6] (see also under Bismuth and Nickel) added to slightly ammoniacal copper solutions gives an intense red-violet color when an oxidizing agent such as a mixture of $AgNO_3$ and ammonium persulfate, $(NH_4)_2S_2O_8$, is added.

p-Dimethyl-amino-benzylidine-rhodanine[7] (see also under Silver and Mercury) gives a purplish-red precipitate with a solution of a cuprous salt (prepared by reducing a cupric salt with neutral sodium sulfite).

Cupric ions greatly accelerate the reduction of ferric salts by sodium thiosulfate.[8] Hence, if a solution containing copper is added to a ferric thiocyanate solution (see the thiocyanate test for iron) to which a dilute solution of sodium thiosulfate, $Na_2S_2O_3$, has been added, this solution will be decolorized, owing to the reduction of the ferric ion, more quickly than a blank test containing no copper. Another reaction in which copper is detected by its catalytic action is the following:[9] Sodium hypobromite, NaBrO, in the presence of copper oxidizes a solution of $MnSO_4$ to $NaMnO_4$, which may be detected by the characteristic permanganate color. In the absence of copper a black precipitate of H_2MnO_3 is obtained.

1,2-Diamino-anthraquinone-3-sulfonic acid[10] gives a blue color which, it is claimed, will permit 1 part of Cu in 8,000,000 of water to be detected.

Some of the other tests that have been proposed involve the use of: *o*-nitrosophenol,[11] pyridine and potassium thiocyanate,[12] the amino acid leucine,[13] naphthenic acid,[14] 8-hydroxyquinoline,[15] rubeanic acid,[16] diphenylthiocarbazone,[17] benzidine[18] or *o*-tolidine, 2,7-diaminofluorene,[19] β-naphthol[20] and many phenol derivatives in the presence of H_2O_2.[21]

[1] F. Ephraim, Ber. **63B**, 1928 (1930); C. A. 5665 (1930). Ber. **64B**, 1215 (1931); C. A. 3590 (1931).

[2] F. Feigl, Ber. **56B**, 2083 (1923); C. A. 30 (1924). Mikrochemie **1**, 74 (1923); C. A. 1624 (1924).

[3] G. Denigès, Bull. soc. pharm. Bordeaux **70**, 101 (1932); C. A. 927 (1933). Compt. rend. **194**, 895 (1932); C. A. 2935 (1932).

[4] F. Ephraim, Ber. **64B**, 1210 (1931); C. A. 3589 (1931).

[5] R. Montequi, Anales soc. españ. fís. quím. **25**, 52 (1927); C. A. 2858 (1927). F. Feigl, Mikrochemie **7**, 10 (1929); C. A. 4421 (1929).

[6] I. M. Kolthoff, J. Am. Chem. Soc. **52**, 2222 (1930); C. A. 3726 (1930).

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[8] F. Hahn and G. Leimbach, Ber. **55B**, 3070 (1922); C. A. 701 (1923). J. Holluta and A. Martini, Z. anorg. allgem. Chem. **140**, 208 (1924); C. A. 789 (1925). F. L. Hahn, Festschr. Physik Ver., Sep. **1924**; C. A. 1573 (1926).

[9] G. Denigès, Bul. soc. pharm. Bordeaux **70**, 179 (1932); C. A. 928 (1933). K. M. Filimonovich, Ukrain. Khem. Zhur. **5**, Sci. Pt., 383 (1930); C. A. 5640 (1931).

[10] G. Gutzeit, Helv. Chim. Acta **12**, 729 (1929); C. A. 4644 (1929). R. Uhlenhuth, Chem.-Ztg. **34**, 887 (1910); C. A. 3178 (1910). J. V. Dubský and V. Bencko, Z. anal. Chem. **94**, 19 (1933); C. A. 5021 (1933).

[11] O. Baudisch and S. Rothschild, Ber. **48**, 1660 (1915); C. A. 196 (1916).

[12] G. Spacu, Bul. soc. stiinte Cluj. **1**, 284 (1922); C. A. 1772 (1923).

[13] Lyle, Curtman and Marshall, J. Am. Chem. Soc. **37**, 1471 (1915); C. A. 1729 (1915).

[14] K. Kharichkov, Chem.-Ztg. **34**, 479 (1910); C. A. 2081 (1910).

[15] R. Berg, Z. anal. Chem. **70**, 341 (1927); C. A. 1778 (1927). E. Cattelain, J. pharm. chim. [8], **11**, 484 (1930); C. A. 894 (1931). J. Calvet, Compt. rend. **195**, 148 (1932); C. A. 4768 (1932). R. Berg and H. Künstenmacher, Z. anorg. allgem. Chem. **204**, 215 (1932); C. A. 2135 (1932).

[16] P. Rây, Z. anal. Chem. **79**, 94 (1929); C. A. 1054 (1930).

[17] H. Fischer, Mikrochemie [N. S.] **2**, 319 (1930); C. A. 893 (1931). H. Fischer, Wiss. Veröff. Siemans-Konz. **4**, 158 (1925); C. A. 3660 (1926).

[18] G. Spacu, Z. anal. Chem. **67**, 31 (1925); C. A. 3444 (1925). F. Feigl and F. Neuber, Z. anal. Chem. **62**, 369 (1923); C. A. 2687 (1923).

[19] A. Folcini, Rev. centro. estud. farm. bioquím. **17**, 305 (1928); C. A. 2689 (1930). J. Schmidt and W. Hinderer, Ber. **64B**, 1793 (1931); C. A. 4813 (1931).

[20] C. Fulton, Am. J. Pharm. **105**, 62 (1933); C. A. 1840 (1933).

[21] C. Fulton, Am. J. Pharm. **105**, 25 (1933); C. A. 1843 (1933).

CADMIUM, Cd^{++}

In the periodic table cadmium falls in the same group as mercury and zinc, and as would be expected, its properties are in many ways similar to those of these two metals. Like mercury, it occurs in both mono- and di-valent states, but the monovalent (cadmous) salts are rare and are not considered here.

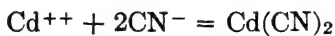
In many of its reactions and salts it resembles zinc, but in its behavior toward the analytical reagents of the cation scheme it closely follows the behavior of copper. Thus, like copper, as shown in the preliminary experiments, the sulfide, CdS, is precipitated by H_2S; Na_2S_2 does not dissolve CdS but nitric acid does; the sulfate is quite soluble, making possible the separation of cadmium from lead; the hydroxide, like that of copper, is soluble in NH_4OH, forming the complex cadmium-ammonia ion $Cd(NH_3)_4^{++}$, this property providing the means of its separation from bismuth.

Separation and Tests for Cadmium

Since cadmium and copper are so closely allied in the scheme of analysis and the usual tests for cadmium are interfered with by copper, the separation of these two elements becomes a matter of considerable analytical importance. The simplest test for cadmium consists in the precipitation with H_2S of yellow CdS, but in the presence of copper, the black color of copper sulfide obscures the yellow color of CdS. Several procedures are available through which the interference of copper can be overcome. The cyanide separation and the hypophosphite separation are here described in detail.

Cyanide Separation.—If a mixture of copper and cadmium ions or of $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ is treated with an excess of KCN, the cupric ion is reduced to the cuprous state and forms the very stable complex cuprous-cyanide ion $Cu(CN)_4^{=}$ (see equations under copper on page 122), whereas the cadmium ion reacts to form a less stable complex cadmium-cyanide ion:

$$Cd^{++} + 2CN^- = \underline{Cd(CN)_2}$$

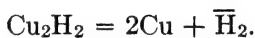
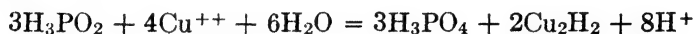
$$\underline{Cd(CN)_2} + 2CN^- = Cd(CN)_4^{=}.$$

The complex cadmium-cyanide ion is dissociated to such an extent that it gives a precipitate of yellow CdS when H_2S is passed into the solution, but the corresponding cuprous-cyanide ion is so slightly dissociated that no Cu_2S is precipitated by H_2S.

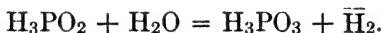
Perform the following experiment: To a solution containing copper and cadmium add dilute NH_4OH until the deep blue color of the complex copper-ammonia ion appears. Add KCN solution

drop by drop until the solution becomes colorless and then pass in H_2S. A yellow precipitate of CdS is obtained. The appearance of this precipitate is usually considered sufficient evidence of the presence of cadmium.

Hypophosphite Separation.[1]—To a mixture of solutions of the two metals add dilute H_2SO_4 until distinctly acid and then sufficient sodium hypophosphite, NaH_2PO_2, solution to double the volume. Heat to boiling for a minute. A precipitate of metallic copper is obtained, the cadmium remaining in solution. It is probable that cuprous hydride is first formed, but is decomposed by heating:[2]

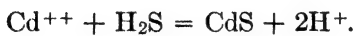
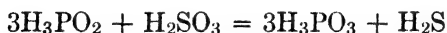
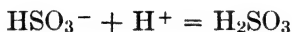
$$3H_3PO_2 + 4Cu^{++} + 6H_2O = 3H_3PO_4 + 2Cu_2H_2 + 8H^+$$

$$Cu_2H_2 = \underline{2Cu} + \overline{H_2}.$$

It is possible, however, that the evolution of hydrogen is caused by the copper sponge (formed without the intermediate formation of the hydride) acting as a catalyst to decompose excess H_3PO_2, set free by the H_2SO_4:

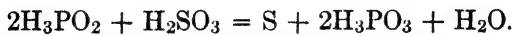
$$H_3PO_2 + H_2O = H_3PO_3 + \overline{H_2}.$$

Centrifuge and remove the clear supernatant solution. To this solution add several drops of sodium bisulfite, $NaHSO_3$, solution. A yellow precipitate of CdS is formed. A dark precipitate indicates incomplete removal of the copper. The reactions are as follows:[3]

$$HSO_3^- + H^+ = H_2SO_3$$

$$3H_3PO_2 + H_2SO_3 = 3H_3PO_3 + H_2S$$

$$Cd^{++} + H_2S = \underline{CdS} + 2H^+.$$

This precipitate is usually sufficient evidence of the presence of cadmium.

At times a white precipitate of sulfur is obtained as a result of the following reaction:

$$2H_3PO_2 + H_2SO_3 = \underline{S} + 2H_3PO_3 + H_2O.$$

A separation based on the use of sodium bicarbonate has been

proposed.[4] This consists in adding to a mixture of copper and cadmium some dilute HCl until very slightly acidic, then a few drops of 10 per cent NH_4Cl solution and finally sufficient saturated $NaHCO_3$ solution to double the volume. White $CdCO_3$ is precipitated. After centrifuging, the precipitate is removed and dissolved in dilute HCl and further identifying tests are applied. If the precipitate is blue ($CuCO_3$), more NH_4Cl must be added and the mixture stirred until the blue color disappears.

Formaldehyde has likewise been suggested;[5] if added to complex cyanides it precipitates $Cd(OH)_2$, leaving the copper in solution. The hydroxide may be dissolved in dilute HCl and confirmatory tests applied.

Other separations involving gallic acid,[6] reduction of the copper with nickel powder[7] and the thermal decomposition of copper formate[8] (cadmium formate is more stable) have been described.

Of the identifying tests for cadmium, aside from the use of H_2S, the following reaction should be tried:

Thiosin-Amine Test.[9]—This reagent is also known as allyl thiourea, $NH_2 \cdot CS \cdot NH(CH_2CH : CH_2)$. To a drop of test solution on a glass slide add a drop of concentrated NaOH solution and then a drop of the reagent solution. Warm gently. A yellow precipitate forms. Care must be taken not to heat too much as a high temperature will cause the formation of a yellow precipitate from the reagent itself. For this reason it is best to place a drop of the reagent itself near the test drop on the same slide and heat the two equally. Copper does not interfere with this test.

Other Identifying Tests

Other tests include the use of diphenyl-carbazide reaction.[10] This is conducted by placing two drops of the diphenyl-carbazide solution, saturated with KCNS, on separate areas of drop-reaction paper and drying. To one spot a drop of test solution is added and then both spots are developed with NH_3. Cadmium gives a violet-blue coloration. Although this test has been recommended for detection of cadmium in the presence of copper, it has been found not to be completely satisfactory.

Dinitrodiphenyl-carbazide[11] turns $Cd(OH)_2$ (precipitated by formaldehyde) a blue color.

Nitrophenol-arsinic acid,[12] $C_6H_3(NO_2)OH\ AsO(OH)_2$, with

acetic acid solutions of cadmium salts gives a crystalline precipitate.

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[2] J. Mellor, Comprehensive Treatise, Vol. VIII, pp. 875 et seq.

[3] J. Mellor, Comprehensive Treatise, Vol. VIII, p. 874.

[4] G. M. Karns, J. Am. Chem. Soc. **48**, 2626 (1926); C. A. 3663 (1926).

[5] K. Heller and P. Krumholz, Mikrochemie **7**, 213 (1929); C. A. 1818 (1930).

[6] P. Das-Gupta and H. Saha, J. Indian Chem. Soc. **8**, 19 (1931); C. A. 2938 (1931).

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[9] G. Gutzeit, Helv. Chim. Acta **12**, 729 (1929); C. A. 4644 (1929).

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[11] K. Heller and P. Krumholz, Mikrochemie, **7**, 217 (1929); C. A. 1818 (1930).

[12] F. Pavelka and E. Kolmer, Mikrochemie [N. S.] **2**, 277 (1930); C. A. 1758 (1931).

EXERCISE.—PRACTICE ANALYSIS OF A MIXTURE CONTAINING MERCURY, LEAD, BISMUTH, COPPER AND CADMIUM.—Prepare a mixture containing Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++} ions by taking two drops of each of these stock test solutions, and placing them in a centrifuge tube. The solution will be about $\frac{1}{2}$ cc. in volume and will contain about 1 mg. of each of these five ions. Test the solution with litmus paper and, if not neutral, make it so with NH_4OH. Then, using methyl orange test paper, add enough dilute HCl to turn the test paper pink. Pass into the solution a rapid stream of H_2S. Allow the precipitated sulfides to settle, and pass in a little more H_2S in order to insure complete precipitation. Centrifuge the mixture, discarding the supernatant liquid.

To the sulfides add a few drops of dilute HNO_3, and gently warm. The residue remaining is HgS and S, the other sulfides having dissolved in the nitric acid. This process has now separated mercury from lead, bismuth, copper and cadmium. Pipet off the supernatant liquid, reserving it for tests for the other ions. To the residue add a crystal of $KClO_3$ and a few drops of concentrated HCl, in order to dissolve the HgS. Boil the solution until chlorine is no longer given off; this can be ascertained by holding a piece of moistened starch-potassium iodide paper in the escaping fumes. The heating must be continued until fresh pieces of test paper no longer give a blue color. This solution of mercuric ion, freed from

Cl_2, should now be tested for mercury by the several tests previously referred to in Group I.

Separation and Confirmation of Lead.—To the solution containing the four ions whose sulfides were dissolved in HNO_3, add a few drops of concentrated H_2SO_4. Boil the solution until dense white fumes of SO_3 are evolved and then add a few drops of water. The white precipitate is lead sulfate, $PbSO_4$. Centrifuge the mixture, and pipet into another centrifuge tube the supernatant liquid which contains Bi^{+++}, Cu^{++} and Cd^{++} ions.

Dissolve the lead sulfate in ammonium acetate and using drop portions of the solution, prove the presence of lead by several of the identifying tests already described.

Separation and Confirmation of Bismuth.—To the solution from which lead has been removed, add concentrated NH_4OH until a white precipitate no longer forms. This precipitate is bismuth hydroxide, $Bi(OH)_3$, and brings about the separation of this element from copper and cadmium, which with the excess of NH_4OH form complex ions, namely deep blue $Cu(NH_3)_4^{++}$ ions and colorless $Cd(NH_3)_4^{++}$ ions. Centrifuge the mixture, removing the solution containing cadmium and copper to another tube.

Portions of the bismuth hydroxide should now be dissolved in the least possible quantity of dilute HCl and tested by the identifying tests previously described.

Separation and Confirmation of Copper and Cadmium.—The detection of copper in the presence of cadmium presents no particular difficulty and besides the almost conclusive evidence in the appearance of the intensely blue color of the ammonia complex ion, there have already been described a number of other distinctive reactions and tests for copper. Drop portions of the solution should therefore be taken and the test reagents for copper applied according to the experiments already discussed under copper. The remainder of the solution should be used for the tests for cadmium.

The similarity in the properties of copper and cadmium and in their behavior toward most reagents makes the identification of cadmium in the presence of copper somewhat difficult. The use of thiosin-amine as a special test reagent for cadmium has not been entirely satisfactory. If a separation must be carried out, the procedures to be used will be found discussed under cadmium.

According to the KCN method of separation, this reagent reduces the cupric ion to the cuprous state, forming $Cu(CN)_4^{=}$,

and with cadmium forms $Cd(CN)_4^{=}$, from the latter of which CdS may be precipitated with H_2S. The hypophosphite and the bicarbonate separations may also be used as alternative methods of treating the mixture of ions in order that an identifying test for cadmium may be applied.

DIAGRAMMATIC SCHEME OF SEPARATION OF GROUP II A

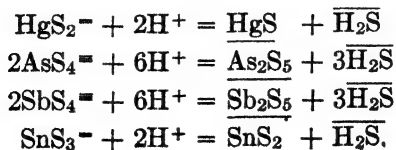
Solution contains:		*Precipitate:*		*Residue:*				
Hg^{++}	Bring to correct acidity, using methyl orange paper. Pass in H_2S	HgS	Add dilute HNO_3	HgS—Dissolve in $KClO_3$+conc. HCl				
				Solution:		*Precipitate:*		
Pb^{++}		PbS		Pb^{++}	Add H_2SO_4	$PbSO_4$—Dissolve in $NH_4C_2H_3O_2$		
						Solution:		*Precipitate:*
Bi^{+++}		Bi_2S_3		Bi^{+++}		Bi^{+++}	Add NH_4OH	$Bi(OH)_3$
								Solution:
Cu^{++}		CuS		Cu^{++}		Cu^{++}		$Cu(NH_3)_4^{++}$
Cd^{++}		CdS		Cd^{++}		Cd^{++}		$Cd(NH_3)_4^{++}$

GROUP II. DIVISION B

Separation of the Ions of Group II B

Experiment 9.—Refer to Experiments 4 and 5 on page 115 and repeat the precipitation with H_2S of the sulfides of mercury, arsenic, antimony and tin, and their solution in Na_2S_2. When polysulfides react with HgS, As_2S_5, Sb_2S_5 and SnS_2, the soluble complex metal thio (or sulfo) ions are formed directly. With As_2S_3, Sb_2S_3 and SnS, there is first an oxidation to the higher state followed by the formation of the complex thio salt. The final result is that HgS may partly dissolve in the Na_2S_2 with the formation of the $HgS_2^{=}$ ion. Both of the sulfides of arsenic yield $AsS_4^{\equiv}$, those of antimony $SbS_4^{\equiv}$ and those of tin $SnS_3^{=}$.

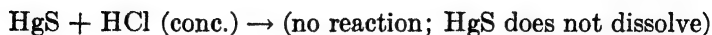
With these dissolved sulfides now in separate test tubes, add to each a few drops of dilute HCl. The mercury reprecipitates as HgS, and the thioarsenate, thioantimonate and thiostannate form, respectively, arsenic pentasulfide, As_2S_5, antimony pentasulfide, Sb_2S_5, and stannic sulfide, SnS_2, in accordance with the equations:

$$HgS_2^{=} + 2H^+ = \underline{HgS} + \overline{H_2S}$$
$$2AsS_4^{\equiv} + 6H^+ = \underline{As_2S_5} + 3\overline{H_2S}$$
$$2SbS_4^{\equiv} + 6H^+ = \underline{Sb_2S_5} + 3\overline{H_2S}$$
$$SnS_3^{=} + 2H^+ = \underline{SnS_2} + \overline{H_2S}.$$

Experiment 10. Separation of Arsenic (and Mercury) from Antimony and Tin.—Centrifuge off each of these sulfides, and to each add several drops of concentrated HCl. Note that As_2S_5 and HgS do not dissolve and that Sb_2S_5 and SnS_2 do, the antimony being at the same time reduced to the Sb^{+++} ion:

$$\underline{HgS} + HCl\ (conc.) \rightarrow \text{(no reaction; HgS does not dissolve)}$$

$$\underline{As_2S_5} + HCl\ (conc.) \rightarrow \text{(no reaction; } As_2S_5 \text{ does not dissolve)}$$

$$\underline{Sb_2S_5} + 6HCl\ (conc.) = 2Sb^{+++} + 3\overline{H_2S} + 6Cl^- + \underline{2S}$$

$$\underline{SnS_2} + 4HCl\ (conc.) = Sn^{++++} + 2\overline{H_2S} + 4Cl^-.$$

No further separation of antimony from tin is necessary in the systematic scheme of analysis.

Properties and Tests, Group II B

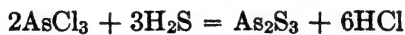
ARSENIC, As^{+++}, $AsO_3^{=}$; As^{+++++}, $AsO_4^{=}$

The element arsenic exists in two valence conditions, the trivalent and the pentavalent. In both states of oxidation there exist cation and anion forms, as for instance, As_2S_3 and H_3AsO_3 in both of which the arsenic is in the trivalent state, and As_2S_5 and H_3AsO_4 both compounds containing arsenic in the pentavalent state. In a solution containing the element in the lower state, as in the arsenious test solution, both As^{+++} and $AsO_3^{=}$ ions are present. Likewise in the test solution containing pentavalent arsenic there are As^{+++++} and $AsO_4^{=}$ ions.

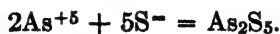
The action of H_2S on trivalent arsenic, as shown in the group precipitation, Experiment 4, is to precipitate yellow arsenious sulfide, according to the equations:

$$2AsCl_3 + 3H_2S = \underline{As_2S_3} + 6HCl$$

and

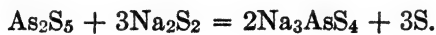
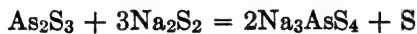
$$2H_3AsO_3 + 3H_2S = \underline{As_2S_3} + 6H_2O.$$

The reactions take place readily and rapidly even in the presence of a considerable concentration of HCl.

The action of H_2S on pentavalent arsenic is slow, and results in a mixture of the two sulfides. A small part of the arsenic is precipitated directly as As_2S_5:

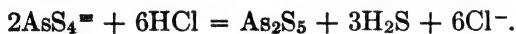
$$2As^{+5} + 5S^{=} = As_2S_5.$$

The remainder of the solution is slowly reduced to the trivalent condition by the reducing action of H_2S after which the trivalent sulfide is precipitated in accordance with the reactions already given. The best conditions for the precipitation are a high acidity and high temperature. The reduction and subsequent precipitation can be hastened by bringing about a preliminary reduction by adding a few crystals of NH_4I, before passing in H_2S.

The sulfides of arsenic are soluble in alkali sulfides, in KOH and NH_4OH and in oxidizing solvents such as HNO_3, $KClO_3$ and concentrated HCl, H_2O_2, etc. The action of sodium or ammonium polysulfide or of potassium hydroxide is utilized in systematic analysis to separate arsenic, together with antimony and tin, from the sulfides of the copper subgroup. Ordinary ammonium or sodium sulfide will react with As_2S_3 and As_2S_5, respectively, to form the soluble complex thio salts, namely, $(NH_4)_3AsS_3$ and $(NH_4)_3AsS_4$. But if the polysulfide reagents, Na_2S_2 or $(NH_4)_2S_2$, are used, the arsenious form becomes oxidized, so that the product is the same in either case:

$$\underline{As_2S_3} + 3Na_2S_2 = 2Na_3AsS_4 + S$$

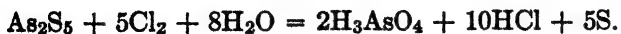
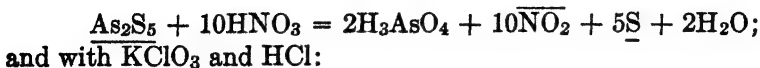
$$\underline{As_2S_5} + 3Na_2S_2 = 2Na_3AsS_4 + 3S.$$

The thioarsenate ion, $AsS_4^{\equiv}$, is analogous to the arsenate ion, $AsO_4^{\equiv}$, in which sulfur has replaced oxygen.

If a solution of a thioarsenate is acidified with dilute HCl, As_2S_5 precipitates:

$$2AsS_4^{\equiv} + 6HCl = \underline{As_2S_5} + 3H_2S + 6Cl^-.$$

Arsenic pentasulfide is not soluble in concentrated HCl, differing in this respect from Sb_2S_5 and SnS_2, a fact used in the separation of arsenic from antimony and tin. It is soluble, however, in oxidizing agents such as strong HNO_3, $KClO_3$ and HCl, H_2O_2 or bromine and in NH_4OH and KOH, yielding a solution containing the $AsO_4^{\equiv}$ ion. With HNO_3 the reaction is:

$$\underline{As_2S_5} + 10HNO_3 = 2H_3AsO_4 + 10\overline{NO_2} + 5\underline{S} + 2H_2O;$$

and with $KClO_3$ and HCl:

$$As_2S_5 + 5Cl_2 + 8H_2O = 2H_3AsO_4 + 10HCl + 5\underline{S}.$$

Tests for Arsenic

There are a number of distinctive tests for arsenic, some of which have been refined to make them applicable to the micro technique. Many of these tests are designed to detect arsenic when in the form of the arsenate ion, in which form the element exists when separated from antimony and tin.

Silver Nitrate Test.—To a drop of neutral $AsO_4^{\equiv}$ test solution on a spot plate, add a drop of $AgNO_3$ solution. The chocolate brown precipitate is silver arsenate:

$$3Ag^+ + AsO_4^{\equiv} = \underline{Ag_3AsO_4}.$$

The precipitate is insoluble in acetic acid. Arsenites, on the other hand, give with silver nitrate a yellow precipitate of silver arsenite, Ag_3AsO_3. This micro test is described by Feigl.[1] It is not very sensitive.

Magnesium Reagent Test.—If magnesia mixture (a solution of $MgCl_2$ and NH_4Cl in NH_4OH solution) is added to an arsenate, a white precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, is formed. The essential ionic reaction is:

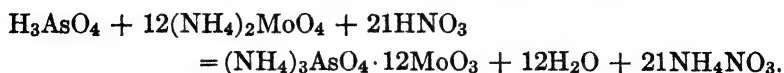
$$Mg^{++} + NH_4^+ + AsO_4^{\equiv} = \underline{MgNH_4AsO_4}.$$

This is an important analytical reaction and is frequently involved in the detection and quantitative determination of arsenic. The phosphate ion, $PO_4^{\equiv}$, behaves in an analogous way.

A similar reaction has been proposed for a micro test.[2] A drop of the solution is first converted, if necessary, into the arsenate form by a double treatment and evaporation with aqua regia, the residue taken up in a drop of water and a concentrated solution of $Mg(NO_3)_2$ added. $MgHAsO_4$, a white precipitate, forms. This test must be performed very carefully as otherwise the result will be unsatisfactory.

Ammonium Molybdate Test.—A characteristic reaction of arsenates is the production of a dense yellow precipitate of ammonium arseno-molybdate, when a nitric acid solution of an arsenate is treated with ammonium molybdate. The product has the approximate composition represented by the formula:

$(NH_4)_3AsO_4 \cdot 12MoO_3$, i.e., a molecule of $(NH_4)_3AsO_4$ to which are attached 12 molecules of molybdic oxide. The reaction is:

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3AsO_4 \cdot 12MoO_3 + 12H_2O + 21NH_4NO_3.$$

The molybdate test may be modified by the following procedure:[3] Place a drop of arsenate test solution on drop reaction paper and add a drop of $(NH_4)_2MoO_4$ solution containing tartaric acid. Warm the spot by placing the paper on a heated wire gauze. A blue color appears after some time.

Gutzeit Test.—This test gives very satisfactory results on the micro scale. It depends upon the liberation of arsine, AsH_3, and its subsequent reaction with $AgNO_3$. Place a few drops of test solution in the evolution tube; add a few granules of zinc (arsenic free) and a drop or two of dilute H_2SO_4. Place over the tube a strip of filter paper which has been moistened with a 1 : 1 solution of $AgNO_3$. A yellow or gray spot will form, due to the double salt, $AsAg_3 \cdot AgNO_3$.

$SnCl_2$ (Bettendorff) Test.—Place two drops of concentrated HCl on a spot plate, add one drop of As^{+++} solution and then one or two drops of a freshly prepared saturated solution of $SnCl_2$ in concentrated HCl. A decided brown color forms in one minute or less. The color is due to the reduction to metallic arsenic. The original test is due to Bettendorff. The test has been made specific by Feigl by treating a drop of the solution to be tested in a micro crucible with one or two drops of NH_4OH, H_2O_2 and saturated $MgCl_2$, slowly evaporating and igniting. This treatment converts the arsenic into $MgNH_4AsO_4$ and finally into $Mg_2As_2O_7$ (magnesium pyroarsenate). The ignited residue is treated with the acidified $SnCl_2$ solution and gently heated, when reduction takes place forming brownish free arsenic. Other modifications have been proposed by Scheucher,[5] by Kolthoff,[6] by Covelli[7] and others.

[1] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 181.

[2] F. Emich, Lehrbuch der Mikrochemie, p. 87.

[3] G. Denigès, Compt. rend. **185**, 777 (1927); C. A. 363 (1928).

[4] A. Polyakov and N. Kolokolov, Biochem. Z. **213**, 375 (1929); C. A. 311 (1930).

[5] H. Scheucher, Monatsh. **42**, 411 (1922); C. A. 2821 (1922).

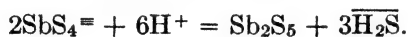
[6] I. Kolthoff, Pharm. Weekblad **59**, 334 (1922); C. A. 3604 (1922).

[7] E. Covelli, Boll. chim. farm. **47**, 635 (1909); C. A. 1890 (1910).

ANTIMONY, Sb^{+++}, $SbO_3^{\equiv}$; Sb^{+++++}, $SbO_4^{\equiv}$

Antimony, like arsenic, forms compounds in which the element is either trivalent or pentavalent, and anion as well as cation forms exist. In antimonous salts and in antimonites, antimony has a valence of +3; in antimonic salts, the valence is +5. Salts of antimony are easily hydrolyzed, like those of bismuth and tin, forming insoluble basic salts such as SbOCl.

Hydrogen sulfide precipitates the orange-colored sulfides Sb_2S_3 and Sb_2S_5. Both sulfides are dissolved by alkali sulfides. Sodium polysulfide, for example, converts both sulfides into sodium thioantimonate, Na_3SbS_4. If a solution of the thioantimonate is acidified with dilute HCl, Sb_2S_5 precipitates:

$$2SbS_4^{\equiv} + 6H^+ = \underline{Sb_2S_5} + 3\overline{H_2S}.$$

Antimony pentasulfide is soluble in concentrated HCl, differing in this respect from As_2S_5. The antimony is at the same time reduced to the trivalent condition:

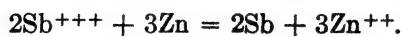
$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3\overline{H_2S} + 2\underline{S}.$$

Tests for Antimony

A number of tests are available for the detection of antimony. In the antimonous form in which it is present when tested for in the analytical scheme, the following tests may be used.

Reduction of Antimony to the Metallic State.—This test is one commonly used in the conventional macro scheme of analysis. On the micro scale [1] the procedure may be carried out as follows:

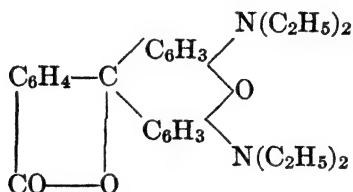
Place a small piece of zinc on the spot plate, place in contact with it a small square of platinum foil or a short piece of platinum wire and then add a drop of the antimony solution acidified with strong HCl. A black coating of metallic antimony forms on the foil:

$$2Sb^{+++} + 3Zn = \underline{2Sb} + 3Zn^{++}.$$

The coating is insoluble in NaOCl solution. As a modification, it has been suggested to replace the platinum by a small square of copper foil. [2]

Sodium Thiosulfate Test. [3]—Place several drops of test solution in a watch glass and heat rapidly to boiling to prevent undue evaporation. Drop a crystal of $Na_2S_2O_3$ into the boiling solution.

A vermilion coating of antimony oxysulfide collects on the crystal. No other ion of Group II gives this test. It is important that the solution be hot when adding the sodium thiosulfate crystal.

Rhodamine B Test.[4]—This test is specific for pentavalent antimony. Since the usual test solution contains trivalent antimony, it must first be oxidized, as follows: Place a drop of solution on the spot plate; add some crystals of KNO_2 and one or two drops of concentrated HCl. When effervescence has ceased add several drops of the reagent. This dye is tetraethylrhodamine, commonly known as rhodamine B, and has the structure

```
                          N(C2H5)2
           /C6H3/
C6H4—C            \
  |     |              >O
  |     |\            /
  |     |  C6H3<
  |     |          N(C2H5)2
CO——O
```

A distinct change in color from bright red to violet occurs. This test is highly recommended by several investigators.

Further Micro Tests for Antimony

Phosphomolybdic Acid Test.—The reagent, prepared by dissolving ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$, in aqua regia, evaporating to dryness and recrystallizing the residue, reacts with a number of cations, by which the molybdenum is reduced to the so-called molybdenum blue. This test was proposed by Feigl and Neuber[5] and may be conducted by placing a drop of the antimony solution on drop-reaction paper and holding the paper in steam. After several minutes the spot becomes blue. In connection with the use of this reagent see also the corresponding test under tin.

Other tests, more or less sensitive, are referred to below. Some of these aim to make the test more specific; others, to effect a better separation from tin, and still others combine the identification with a quantitative estimation.

Clarke[6] recommends the use of potassium iodide and pyridine in a strongly acid solution, which with antimony gives a yellow color. This test can be conducted in the presence of arsenic and tin. Caille and Viel,[7] on the other hand, recommend potassium

iodide and antipyrine, the mixture giving a yellow precipitate. A tiny crystal of CsCl and one of KI added to a drop of antimonous solution give a deep red precipitate.[8]

Various modifications of the luminescence test have recently been described. The test consists, according to Paneth and Winternitz,[9] in igniting the gas issuing from the Marsh apparatus and allowing the flame to impinge on a piece of pure $CaCO_3$, giving a deep blue color. Scheucher[10] dissolves the visible or invisible Marsh mirrors in HNO_3, transfers to pure $CaCO_3$ and heats with the Bunsen flame.

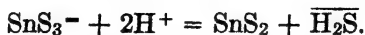
[1] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 183.
[2] P. Haferkorn, Chem.-Ztg. **46**, 186 (1922); C. A. 1545 (1922).
[3] V. Njegovan, Chem.-Ztg. **45**, 681 (1921); C. A. 3429 (1921).
[4] E. Eegriwe, Z. anal. Chem. **70**, 400 (1927); C. A. 1779 (1927).
[5] F. Feigl and F. Neuber, Z. anal. Chem. **62**, 369 (1923); C. A. 2687 (1923).
[6] S. Clarke, Analyst **53**, 373 (1928); C. A. 3369 (1928).
[7] Caille and E. Viel, Compt. rend. **176**, 1759 (1923); C. A. 3518 (1923).
[8] F. Emich, Lehrbuch der Mikrochemie, p. 88.
[9] F. Paneth and E. Winternitz, Ber. **51**, 1728 (1918); C. A. 1431 (1919).
[10] H. Scheucher, Monatsh. **42**, 411 (1922); C. A. 2821 (1922).

TIN, Sn^{++} and Sn^{++++}

Tin forms two series of compounds, the stannous in which the tin is divalent, and the stannic which contains tetravalent tin. Tin is quite easily changed from one form to the other by oxidizing or reducing agents.

Hydrogen sulfide, as shown by Group Experiment 4, precipitates yellow stannous sulfide, SnS, from stannous solutions and brown stannic sulfide, SnS_2, from solutions containing stannic tin. The sulfides are soluble in alkali sulfides and polysulfides, Na_2S_2, producing the thiostannate ion, $SnS_3^{=}$.

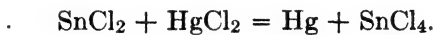
Stannic sulfide is easily reprecipitated from solutions of the thiostannate by the action of dilute HCl:

$$SnS_3^{=} + 2H^+ = \underline{SnS_2} + \overline{H_2S}.$$

SnS_2 like Sb_2S_5 is soluble in concentrated HCl, forming $SnCl_4$ or H_2SnCl_6 (chlorostannic acid). All the tests for the identification of tin depend upon the properties of the stannous ion; therefore, if the ion is in the stannic condition, it must be reduced before applying the tests. This reduction is conveniently effected

by making the stannic solution acidic with dilute HCl and adding a little magnesium powder.

Tests for Tin

Mercuric Chloride Test.—This is the reverse of the $SnCl_2$ test for mercury and may be accomplished by placing two drops of stannous chloride solution on a glass slide and adding a drop of $HgCl_2$ solution. A white precipitate which soon turns gray or black is formed:

$$SnCl_2 + HgCl_2 = \underline{Hg} + SnCl_4.$$

Tananaev[1] has modified this test in the following manner, making it adaptable as a more sensitive micro test. A piece of filter paper is saturated with a concentrated solution of mercuric chloride. After drying, a drop of the stannous solution is added and then a drop of aniline. A black or brown spot of metallic mercury results.

Cacothelin Test.—Place a drop of cacothelin solution on drop-reaction paper and allow the paper to dry a little, but not completely. Then place a drop of Sn^{++} solution in the center of the spot. A lavender color appears. No ions of Group II interfere with this test. This test was first described by Gutzeit.[2] Care must be taken to employ a fresh solution of the reagent.

Flame Coloration Test.[3]—Place two drops of Sn^{++} solution on a spot plate; add a drop of dilute HCl and a piece of zinc. Have ready a micro crucible filled with cold water, and stand it in the solution. After a short time pick up the crucible with forceps and hold it in a colorless micro flame. If the bottom of the crucible is closely observed a blue flame, due to the burning of tin hydride, will be seen to play about it. The eye should be on a level with the bottom of the crucible in making the observation.[4,5,6]

Additional Tests for Tin

Phosphomolybdic acid,[7,8,9] if placed on a strip of filter paper, developed with NH_3, dried and then touched with a drop of stannous solution, will yield a blue color, the so-called molybdenum blue. This test, which is interfered with under certain conditions by antimony, was proposed by Feigl and Neuber.

Dimethylglyoxime, the favorite reagent for nickel, can be

employed as a test for tin by the following procedure: To a drop of strongly acid stannous test solution on a spot plate add a drop of dilute $FeCl_3$ solution. After standing for one minute add a small crystal of tartaric acid, and when this has dissolved neutralize the solution with dilute NH_4OH. A red color appears.[10]

Eegriwe[11] suggests the use of the dye, diazine green S(K), which gives a reddish or violet color with a reduced tin solution.

Other reagents and methods suggested are the following: Potassium iodide will form yellow crystals of SnI_2 or SnI_4 at the junction formed by a tin solution and one of concentrated H_2SO_4.[12, 13] Resorcinol,[14] cupferron[15] and sodium alizarin sulfonate[16] have likewise been proposed as tests for tin.

[1] N. A. Tananaev, Z. anorg. allgem. Chem. **133**, 372 (1924); C. A. 1628 (1924).

[2] G. Gutzeit, Helv. Chim. Acta **12**, 720 (1929); C. A. 4644 (1929). L. Newell, J. Ficklen and L. Maxfield, Ind. Eng. Chem., Anal. Ed. **7**, 26 (1935); C. A. 1356 (1935).

[3] H. Meissner, Z. anal. Chem. **80**, 247 (1930); C. A. 3966 (1930).

[4] I. Stone, Chemist Analyst **20**, No. 2, 6 (1931); C. A. 1758 (1931).

[5] E. Schröer and A. Balandin, Z. anorg. allgem. Chem. **189**, 258 (1930); C. A. 3458 (1930).

[6] F. L. Hahn, Z. anal. Chem. **82**, 113 (1930); C. A. 51 (1931).

[7] F. Feigl and F. Neuber, Z. anal. Chem. **62**, 382 (1923); C. A. 2687 (1923).

[8] G. F. Hüttig, Chem.-Ztg. **47**, 341 (1923); C. A. 2249 (1923).

[9] L. A. Munro, Proc. Trans. Nova Scotian Inst. Sci. **16**, 9 (1928); C. A. 2872 (1928).

[10] F. Feigl, Chem.-Ztg. **43**, 861 (1919); C. A. 1274 (1920).

[11] E. Eegriwe, Z. anal. Chem. **74**, 225 (1928); C. A. 3859 (1928).

[12] A. Mazuir, Ann. chim. anal. chim. appl. **2**, 9 (1920); C. A. 1091 (1920).

[13] H. Heller, Z. anal. Chem. **57**, 180 (1922); C. A. 3043 (1922).

[14] L. Bey, Bull. soc. chim. [4] **47**, 1192 (1930); C. A. 1761 (1931).

[15] P. Agostini, Ann. chim. applicata **19**, 164 (1929); C. A. 5431 (1929).

[16] F. Germuth and C. Mitchell, Am. J. Pharm. **101**, 46 (1929); C. A. 1366 (1929).

Exercise. Practice Analysis of a Mixture Containing Arsenic, Antimony and Tin.—For such an artificial mixture it is recommended that a few drops of the $AsO_3^{\equiv}$, the Sb^{+++} and the Sn^{++} stock test solutions be taken. Place the mixture in a centrifuge tube, dilute with an equal volume of water, warm and saturate with H_2S. The sulfides formed are As_2S_3, Sb_2S_3 and SnS. Centrifuge, and remove the supernatant liquid.

To the mixed sulfides add a few drops of Na_2S_2 solution, warm-

ing the mixture until complete solution takes place. The dissolved precipitates are now in the form of Na_3AsS_4, Na_3SbS_4 and Na_2SnS_3. To this solution add dilute HCl. This results in the precipitation of As_2S_5, Sb_2S_5 and SnS_2. Remove the supernatant liquid and now add two or three drops of concentrated HCl to the residue, boil and then dilute with several drops of water. Centrifuge. The residue consists of undissolved As_2S_5 and sulfur. The solution contains Sb^{+++} and Sn^{++++} ions.

After washing the residue with water add some dilute NH_4OH which will dissolve the arsenic sulfide. The solution may now be tested for $AsO_4^{\equiv}$ ion by the methods suggested as tests for the arsenate ion.

The tests for antimony and tin are made in the solution obtained from the concentrated HCl treatment of the mixed sulfides. For the purpose of showing the presence of antimony, portions of the solution should be withdrawn and individually treated according to the procedures described as tests for antimony.

The test reagents for tin are likewise applied to drop portions of the solution and the presence of tin shown in the mixture.

DIAGRAMMATIC SCHEME OF SEPARATION OF GROUP II B

Solution contains:		*Precipitate:*		*Solution:*		*Precipitate:*		*Residue:*
$AsO_3^{\equiv}$	Acidify with HCl. Pass in H_2S.	As_2S_3	Na_2S_2	$AsS_4^{\equiv}$	Dilute HCl	As_2S_5	Conc. HCl	As_2S_5
Sb^{+++}		Sb_2S_3		$SbS_4^{\equiv}$		Sb_2S_5		*Solution:* Sb^{+++}
Sn^{++}		SnS		$SnS_3^{=}$		SnS_2		Sn^{++++}

GROUP III. THE AMMONIUM HYDROXIDE AND AMMONIUM SULFIDE GROUP

IRON, Fe^{+++}
MANGANESE, Mn^{++}
ALUMINUM, Al^{+++}
CHROMIUM, Cr^{+++}
NICKEL, Ni^{++}
COBALT, Co^{++}
ZINC, Zn^{++}

Group Precipitation and Separation

Experiment 11. Action of NH_4OH and Separation of Fe, Mn, Al and Cr from Ni, Co and Zn.—In separate centrifuge tubes

place two drops each of the test solutions of Fe^{+++}, Mn^{++}, Al^{+++}, Cr^{+++}, Ni^{++}, Co^{++} and Zn^{++}. Carefully add dilute NH_4OH to each until the precipitates which form persist. The result is that, in each tube, insoluble hydroxides are formed with an equivalent amount of NH_4OH. Then to each tube add an excess of the base, shaking or stirring the tubes during the treatment. It will be observed that in the cases of nickel, cobalt and zinc the hydroxides dissolve, while those of iron, manganese, aluminum and chromium remain undissolved. The action of the excess of NH_4OH is to form complex metal-ammonia ions in those cases in which the hydroxides dissolve. The effect of an equivalent amount and of an excess of NH_4OH on these ions is summarized below.

Ion	*Equivalent NH_4OH*	*Excess NH_4OH*
Fe^{+++}	$Fe(OH)_3$	$Fe(OH)_3$
Mn^{++}	$Mn(OH)_2$	$Mn(OH)_2$
Al^{+++}	$Al(OH)_3$	$Al(OH)_3$
Cr^{++}	$Cr(OH)_3$	$Cr(OH)_3$
Ni^{++}	$Ni(OH)_2$	$Ni(NH_3)_4^{++}$
Co^{++}	$Co(OH)_2$	$Co(NH_3)_6^{+++}$
Zn^{++}	$Zn(OH)_2$	$Zn(NH_3)_4^{++}$

This reagent therefore serves to separate iron, aluminum, chromium completely and manganese almost completely, from nickel, cobalt and zinc. This is the method which will be employed in the microchemical scheme of separation. The first four members are designated as Group IIIA, and the other three as Group IIIB. Reserve the precipitates for use in Experiment 12.

Experiment 12. Action of NaOH.—In separate centrifuge tubes place a few drops each of the test solutions comprising this group. To each tube add NaOH solution drop by drop. A precipitate will be seen to form in each tube. As with the NH_4OH reagent, these precipitates are the hydroxides. To each tube add still more NaOH and note that in the cases of aluminum, chromium and zinc the precipitated hydroxides dissolve, owing to the ampho-

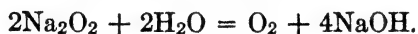
teric nature of these three hydroxides. The effect of an equivalent and of an excess of NaOH is here tabulated.

Ion	*Equivalent NaOH*	*Excess NaOH*
Fe^{+++}	$\underline{Fe(OH)_3}$	$\underline{Fe(OH)_3}$
Mn^{++}	$\underline{Mn(OH)_2}$	$\underline{Mn(OH)_2} \rightarrow MnO(OH)_2$
Ni^{++}	$\underline{Ni(OH)_2}$	$\underline{Ni(OH)_2}$
Co^{++}	$\underline{Co(OH)_2}$	$\underline{Co(OH)_2}$
Al^{+++}	$\underline{Al(OH)_3}$	$Na_3AlO_3 \rightarrow NaAlO_2$
Cr^{+++}	$\underline{Cr(OH)_3}$	$Na_3CrO_3 \rightarrow NaCrO_2$
Zn^{++}	$\underline{Zn(OH)_2}$	Na_2ZnO_2

The manganous hydroxide gradually undergoes oxidation by atmospheric oxygen, the product being indefinite in its composition and the formulas $MnO(OH)_2$, $MnO_2 \cdot 2H_2O$ and Mn_2O_3 being variously assigned to it. To indicate this oxidation product the formula $MnO(OH)_2$ will hereafter be employed. Sodium aluminate undergoes a change, the final product being sodium meta-aluminate, $NaAlO_2$, which yields the AlO_2^- ion. Sodium chromite also becomes sodium metachromite, having in solution the CrO_2^- ion. The zincate ion, ZnO_2^-, forms in the case of the dissolved zinc hydroxide.

It will be observed that in using NaOH the ions of aluminum, chromium and zinc can in this manner be separated from iron, manganese, nickel and cobalt.

Experiment 13.—Repeat Experiment 12, using sodium peroxide, Na_2O_2, instead of NaOH. Na_2O_2 when placed in water decomposes, forming oxygen and NaOH according to the reaction:

$$2Na_2O_2 + 2H_2O = O_2 + 4NaOH.$$

The effect of this reagent on the test solutions is that of the combined action of an excess of NaOH and a vigorous oxidation. The $Mn(OH)_2$ is quickly oxidized to $MnO(OH)_2$. The sodium metachromite, $NaCrO_2$, is oxidized to sodium chromate, Na_2CrO_4, which remains soluble along with the meta-aluminate and zincate ions.

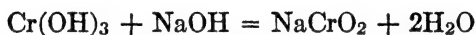
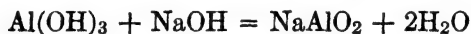
Comparing the results of Experiment 11 with Experiments 12

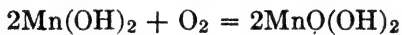
and 13 it is seen that a division into two subgroups can be made either through the action of an excess of NH_4OH, the formation of complex ions of nickel, cobalt and zinc being the basis of separation; or, as revealed in Experiments 12 and 13, through the action of NaOH, preferably accompanied by the oxidizing action of Na_2O_2. The first method is used in the scheme developed for this micro analysis. This makes the action of NaOH or of Na_2O_2 unimportant so far as their effect on Ni^{++}, Co^{++} and Zn^{++} are concerned since these ions are held in solution as ammonia complexes. The use of Na_2O_2, however, is involved in the further separation of iron and manganese from aluminum and chromium. The following experiment has a more direct bearing on the method of separation.

Experiment 14. Separation of Aluminum and Chromium from Iron and Manganese.—Centrifuge off the residues of $Fe(OH)_3$, $MnO(OH)_2$, $Al(OH)_3$ and $Cr(OH)_3$ obtained in Experiment 11. To each residue add two or three drops of water, then the same quantity of NaOH solution. Finally, carefully add some solid Na_2O_2. The mixture effervesces, and the $Al(OH)_3$ and $Cr(OH)_3$ pass into solution, the chromium being oxidized by the oxygen from the Na_2O_2 to the chromate form:

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

$$Cr(OH)_3 + NaOH = NaCrO_2 + 2H_2O$$

$$4NaCrO_2 + 3O_2 + 4NaOH = 4Na_2CrO_4 + 2H_2O.$$

The $Mn(OH)_2$ is oxidized to $MnO(OH)_2$ which still remains as a precipitate:

$$\underline{2Mn(OH)_2} + O_2 = \underline{2MnO(OH)_2}$$

and the $Fe(OH)_3$ is unaffected.

Properties and Tests—Group III A

IRON, Fe^{++} and Fe^{+++}

Iron may be either divalent or trivalent. Ferrous salts are easily oxidized to the ferric condition and are not frequently encountered in an ordinary qualitative analysis, although it sometimes becomes necessary to test for the presence of the ferrous ion. Most of the common tests for iron depend upon the reactions of the ferric ion.

General Properties.—The preliminary experiments have shown that (1) ferric hydroxide, $Fe(OH)_3$, is precipitated by both NH_4OH and NaOH. The hydroxide is not soluble in an excess of either reagent. This shows that complex ammonia ions are not formed with an excess of NH_4OH, and that the ferric hydroxide is not highly amphoteric. (2) Ammonium sulfide (or H_2S in an ammoniacal solution) will precipitate FeS and Fe_2S_3 respectively from solutions containing ferrous and ferric ions. Both sulfides are soluble in dilute HCl.

Tests for Iron

Action of Ferrocyanides and Ferricyanides on Ferrous and on Ferric Salts.—Try the action of a drop of potassium ferrocyanide, $K_4Fe(CN)_6$, and of a drop of potassium ferricyanide, $K_3Fe(CN)_6$, on freshly prepared solutions of $FeSO_4$ and $FeCl_3$. The results are tabulated below.

Reagent	Fe^{++}	Fe^{+++}
$K_4Fe(CN)_6$	White precipitate changing to blue	Prussian blue, $Fe_4[Fe(CN)_6]_3$
$K_3Fe(CN)_6$	Turnbull's blue, $Fe_3[Fe(CN)_6]_2$	Brown solution

The Prussian blue test is a test for ferric ions, and the reagent is potassium **ferrocyanide.** The test for ferrous ions is the formation of Turnbull's blue and is made with potassium **ferricyanide.** Two other tests for iron described below should be tried.

Thiocyanate Test.—Place a drop of ferric test solution on a spot plate and add a drop of NH_4CNS or KCNS solution. A dark-colored solution is formed. Wash the solution into a beaker and dilute the solution with water. A characteristic blood-red color will appear. This test is extremely sensitive. The color was formerly believed to be due to the formation of non-ionized $Fe(CNS)_3$ molecules, but it is now known to be due to a complex anion of the probable formula $Fe(CNS)_6^{\equiv}$. This well-known test for iron has been advocated on the micro scale by Heller and Krumholz.[1]

Sulfosalicylic Acid Test.—This reagent is very sensitive and will detect extremely small amounts of ferric ion.[2] Place a drop of the reagent, a 5 per cent solution of $C_6H_3 \cdot OH \cdot COOH \cdot SO_3H$ in water, on drop-reaction paper and add a drop of the test solution.

A violet color appears. No other ions of Groups III or IV interfere with this test.

Other Tests for Iron

Gutzeit recommends the use of chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid. The test is conducted on a spot plate, a green color being produced. $SnCl_2$ will discharge the color. This is a specific test for iron and is not interfered with by any other ion of this or the following group.

Dimethylglyoxime, the familiar test reagent for nickel, may also be employed as a test for ferrous ions, the test being conducted on a spot plate or drop-reaction paper.[3] The ferrous salt of this reagent has a deep red color. Ferric ions do not give this test; nickel interferes with it.

Among the many tests recently proposed for iron the following may be briefly mentioned. Di-isonitroso-acetone[4] gives with the ferrous ion an intensely blue color and is recommended as an extremely delicate test for divalent iron. Ferric salts must be reduced, preferably with hydrazine, before the test is applied. Cobalt and nickel prevent the color formation, and manganese lessens the intensity.

Dinitroso resorcinol has been suggested by Nichols and Cooper[5] as a test for ferrous ion.

Denigès' reagent, alloxantine, [6,7] produces a blue color with ferric iron, said to be very sensitive and to give positive results in the presence of tartaric and citric acid where the thiocyanate test fails.

Thioglycolic[8] acid gives a red coloration; protocatechuic[9] acid also yields a red color in a slightly alkaline solution; formaldoxime,[10] a violet-red color after several minutes.

Recently Feigl and Hamburg[11] have described the use of α,α'-bipyridyl as an extremely sensitive and specific spot test for ferrous iron. The pink color is due presumably to a complex cation.

[1] K. Heller and P. Krumholz, Mikrochemie **7**, 219 (1929); C. A. 1818 (1930).
[2] L. Moser, A. Brukl and I. Ven, Ber. **58B**, 380 (1925); C. A. 1234 (1925).
[3] L. Chugaev and B. Orelkin, Z. anorg. Chem. **89**, 401 (1914); C. A. 1442 (1915); see also C. A. 1717 (1922), 2634 (1927) and 3931 (1931).
[4] J. Dubský and M. Kuraš, Chem. Listy **23**, 496 (1929); C. A. 801 (1930).

[5] M. Nichols and S. Cooper, J. Am. Chem. Soc. **47**, 1268 (1925); C. A. 1833 (1925).
[6] G. Denigès, Compt. rend. **180**, 519 (1925); C. A. 1674 (1925).
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[8] E. Lyons, J. Am. Chem. Soc. **49**, 1916 (1927); C. A. 3581 (1927).
[9] O. Crutz, Chem.-Ztg. **31**, 570 (1907); C. A. 242 (1908).
[10] G. Denigès, Bull. soc. pharm. Bordeaux **70**, 101 (1932); C. A. 927 (1933).
[11] F. Feigl and H. Hamburg, Z. anal. Chem. **86**, 1 (1931); C. A. 5866 (1931).

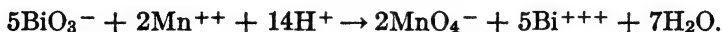
MANGANESE, Mn^{++}

The element manganese appears in a variety of forms in its compounds. In manganous salts, such as $Mn(NO_3)_2$, $MnSO_4$ and MnS, the valence of the element is +2. In manganic salts it is +3. Manganese undergoes a number of oxidation changes. Thus Mn^{++} is easily oxidized to the tetravalent forms, giving such compounds as MnO_2, $MnO(OH)_2$, etc. Further oxidation may yield manganates such as Na_2MnO_4, and complete oxidation results in the formation of permanganates, the most familiar salt being potassium permanganate, $KMnO_4$.

The preliminary experiments have shown that NH_4OH and NaOH yield the hydroxide $Mn(OH)_2$, which is gradually oxidized in the air to a basic oxide of the probable composition $MnO(OH)_2$ or H_2MnO_3. The hydroxide is somewhat soluble in bases, but does not form the complex ammonia ion nor a soluble amphoteric form. Na_2O_2 rapidly oxidizes the manganous ion to the basic oxide. $(NH_4)_2S$ precipitates MnS which gradually becomes oxidized to the basic oxide.

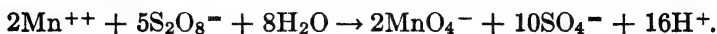
Tests for Manganese

Sodium Bismuthate Test.—Place a drop of test solution on the spot plate. Add a drop of concentrated HNO_3 and then some solid sodium bismuthate, $NaBiO_3$. The purple color of the permanganate ion appears. The reaction is:

$$5BiO_3^- + 2Mn^{++} + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{+++} + 7H_2O.$$

If the solution is so dark that the color cannot be detected, dilute the mixture with water until the color appears. No cations of Groups III–V interfere, but colored ions make detection somewhat difficult.

Ammonium Persulfate Test.—Place a drop of test solution in a micro crucible; add a drop of concentrated H_2SO_4, then one of

$AgNO_3$ solution and then a little solid ammonium persulfate $(NH_4)_2S_2O_8$. Heat gently. The reaction is:

$$2Mn^{++} + 5S_2O_8^{=} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{=} + 16H^{+}.$$

The characteristic color of the permanganate ion appears and may be made more distinctive by diluting with water. This test is not given by any other cation, but anions that precipitate silver salts interfere.

Lead peroxide[1] is frequently used for the oxidation of manganese to the permanganate state. Sodium or potassium periodate[2] has also been suggested for this purpose.

Tetramethyl-diamino-diphenyl-methane, the reagent recommended for lead, can be used successfully as a sensitive test for manganese, the color developed being blue. Ferrous ion gives a green color and is the only ion of Groups III–V which interferes.

Other Tests for Manganese

Benzidine Test.—Feigl[3] and Sensi and Testori[4] recommend this test. The reagent is $C_6H_4NH_2 \cdot NH_2C_6H_4$. To a drop of test solution on drop-reaction paper is added a drop of concentrated NaOH solution. When the drop has stopped spreading, a drop of tartaric acid solution and then one of the reagent are added. A blue color appears. Chromates give the same test.

[1] H. Bösche, Chem.-Ztg. **49**, 378 (1925); C. A. 2180 (1925).

[2] H. H. Willard and L. H. Greathouse, J. Am. Chem. Soc. **39**, 2366 (1917); C. A. 3189 (1917).

[3] F. Feigl and R. Stern, Z. anal. Chem. **60**, 24 (1921); C. A. 2599 (1921).

[4] G. Sensi and R. Testori, Ann. chim. applicata **19**, 383 (1929); C. A. 1053 (1930).

ALUMINUM, Al^{+++}

Aluminum is a trivalent element. The ion, Al^{+++}, is colorless. The hydroxide, $Al(OH)_3$, is colorless and gelatinous. It dissolves in NaOH to form sodium meta-aluminate according to the reaction:

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

Many of the salts of aluminum hydrolyze to form $Al(OH)_3$. For this reason H_2S and $(NH_4)_2S$ precipitate the hydroxide instead of the sulfide. A number of distinctive tests for aluminum depend upon the ability of the hydroxide to adsorb certain dyestuffs

(mordant action) forming characteristically colored adsorption compounds known as " lakes."[1]

Tests for Aluminum

Three lake tests are here described.

1. Alizarin Test.—This test, on a micro scale, has been described by Feigl and Stern.[2] Alizarin, $C_{14}H_6O_2(OH)_2$, forms a bright red color with $Al(OH)_3$. As a micro test, impregnate a strip of filter paper with an alcoholic solution of alizarin, add a drop of the test solution and develop with NH_3 fumes, or else add a speck of the precipitated $Al(OH)_3$.

2. Alizarin-S Test.—The reagent, the sodium salt of alizarinsulfonic acid, as a test for aluminum was proposed by Atack[3] and described as a micro test by Heller and Krumholz.[4] When a drop of the test solution is brought into contact with filter paper impregnated with the reagent and held in NH_3 fumes, a bright red lake forms. A number of other ions will also give the same color, but if the spot is treated with dilute $HC_2H_3O_2$, a brownish-red stain will remain in the presence of aluminum.

3. Aluminon Test.—"Aluminon" is the trade name for the ammonium salt of aurin tricarboxylic acid, $C_{22}H_{14}O_9$, and like alizarin and alizarin-S, will give a red lake with aluminum salts. This reagent was proposed by Hammett and Sottery[5] and is widely used as a test for aluminum in the usual schemes of analysis.

Other Sensitive Tests

Morin, a coloring matter in the extract of fustic wood, was found by Goppelsroeder, as long ago as 1867, to give a green fluorescence with even very small traces of aluminum. This test has been revived by Schantl,[6] Eegriwe and a number of other microchemists, as a sensitive micro test.

Hahn[7] proposes the use of quinalizarin; Eegriwe, the use of the dye eriochrom cyanin R, and Kershner and Duff,[8] the use of purpurin. Details for conducting these newer tests may be found in the original literature.

[1] E. Eegriwe, Z. anal. Chem. **76**, 438 (1929); C. A. 2901 (1929).

[2] F. Feigl and R. Stern, Z. anal. Chem. **60**, 9 (1921); C. A. 2598 (1921).

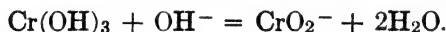
[3] F. Atack, J. Soc. Chem. Ind. **34**, 936 (1915); C. A. 3186 (1915).

[4] K. Heller and P. Krumholz, Mikrochemie **7**, 221 (1929); C. A. 1818 (1930).
[5] L. Hammett and C. Sottery, J. Am. Chem. Soc. **47**, 142 (1925); C. A. 796 (1925).
[6] E. Schantl, Mikrochemie **2**, 174 (1924); C. A. 1108 (1925).
[7] F. Hahn, Mikrochemie [N. S.] **5**, 33 (1932); C. A. 3747 (1932).
[8] K. Kershner and R. Duff, J. Chem. Education **9**, 1271 (1932); C. A. 4007 (1932).

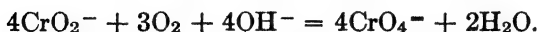
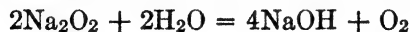
CHROMIUM, Cr^{+++}

The element chromium occurs usually as chromous Cr^{++}, chromic Cr^{+++}, metachromite CrO_2^-, chromate $CrO_4^=$ or dichromate $Cr_2O_7^=$ ion, but it also exists in hepta- and possibly penta-valent forms. The chromous (Cr^{++}) ion is not considered here, and the metachromite (CrO_2^-) ion is considered only incidentally. Solid chromic salts may be green, violet, blue or pink in color, but in solution they are all deep green or, infrequently, violet. The green color in solution may be due to the Cr^{++} ion but is more probably due to a complex ion of the type $[Cr(H_2O)_4Cl_2]^+$. Because of their complex nature chromic salts often behave abnormally in reactions, as in the frequent failure of $BaSO_4$ to precipitate when $BaCl_2$ is added to a solution of chromic sulfate.

From solutions of chromic salts, NH_4OH causes the precipitation of the pale green chromic hydroxide, $Cr(OH)_3$. As with aluminum, the hydroxide is also obtained by the action of $(NH_4)_2S$ due to hydrolysis. $Cr(OH)_3$ dissolves readily in strong bases, forming a grass-green solution containing the chromite, CrO_2^-, ion:

$$Cr(OH)_3 + OH^- = CrO_2^- + 2H_2O.$$

Chromites in basic solution are readily oxidized by sodium peroxide, Na_2O_2, and certain other oxidizing agents, to the chromate ion, $CrO_4^=$, with a change in color from green to yellow:

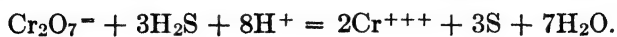
$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

$$4CrO_2^- + 3O_2 + 4OH^- = 4CrO_4^= + 2H_2O.$$

By acidifying a chromate solution, a dichromate, $Cr_2O_7^=$, is formed and the color changes from yellow to orange-red; the reverse change is produced upon making a dichromate solution basic:

$$2CrO_4^= + 2H^+ = Cr_2O_7^= + H_2O$$

$$Cr_2O_7^= + 2OH^- = 2CrO_4^= + H_2O.$$

Chromates and dichromates in an acidic solution are reduced to chromic salts by H_2S, SO_2 and other reducing agents:

$$Cr_2O_7^{=} + 3H_2S + 8H^+ = 2Cr^{+++} + \underline{3S} + 7H_2O.$$

The presence of appreciable quantities of chromium in a solution is usually indicated by the green or yellow color of the solution. All the common tests for identifying chromium depend upon the properties of the chromate and dichromate ions, so that if the element is present in the chromic condition it must first be oxidized. For the following tests the chromic test solution may be used after first oxidizing it by adding NaOH and Na_2O_2, but it is more convenient to use a solution of K_2CrO_4.

Tests for Chromium

Formation of Insoluble Chromates.—To a drop of chromate solution on a spot plate add a drop of $Pb(NO_3)_2$ solution. A yellow precipitate of $PbCrO_4$ forms. If $BaCl_2$ solution is used instead of $Pb(NO_3)_2$ a light yellow precipitate of $BaCrO_4$, which is soluble in strong acids, is obtained. $AgNO_3$ precipitates red Ag_2CrO_4. Compare these reactions with the chromate tests for silver, lead and barium.

Perchromic Acid Test.—To a drop of $CrO_4^{=}$ test solution on a spot plate add a drop of dilute HNO_3 and a drop of 3 per cent H_2O_2 solution. A transient blue color appears, due to the formation of perchromic acid, $H_3CrO_8 \cdot 2H_2O$ or $(OH)_4Cr(O \cdot OH)_3$. If the test is carried out in a test tube containing a few drops of ether, the blue color passes into the ether layer and will then remain for a much longer time.

Additional Proposed Tests

The following tests using organic reagents have recently been described in the chemical literature, all of them depending upon the oxidizing action of the chromate or dichromate ions.

Diphenyl-Carbazide Test.—The reagent is the same as that used in the test for mercury. Place a drop of chromate test solution on drop-reaction paper, acidify with dilute H_2SO_4 and add a drop of the reagent solution. A violet color appears.[1, 2, 3]

Gutzeit[4] recommends the use of α-naphthylamine as a test for the chromate ion. Employing either the spot plate or drop-

reaction paper, the test is conducted by acidifying the chromate solution with concentrated HCl and adding a drop of the reagent, which consists of a saturated solution of the compound in alcohol. A violet spot on the plate, or a brown stain bordered with violet on the paper, is a specific test for chromates. A decided color change must be obtained since several other ions give a slightly brownish color.

Chromotropic acid, 1,8-dihydroxy-naphthalene-3,6-disulfonic acid, has also been suggested as a test. The reagent is an aqueous solution. A drop of this placed on drop-reaction paper and developed with NH_3 fumes, then treated with a drop of dilute H_3PO_4 and finally a drop of the test solution, will yield a brick-red or brown stain. Iron and several other ions interfere with the test.[4]

Another test is with the use of orcin.[4] The compound is *sym*-dihydroxy-toluene and is used as an alcoholic solution. On drop-reaction paper, a drop of the reagent acidified with concentrated HCl and treated with a chromate solution will give a brown stain. The test appears to be more specific than some of the other tests but is not as sensitive.

Other reagents suggested are acid alizarin RC,[5] benzidine,[6] serichrome blue R[7] and the dimethylether of pyrogallic acid.[8]

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[6] N. Tananaev, Z. anorg. allgem. Chem. **140**, 327 (1924); C. A. 1108 (1925).
[7] G. Spencer, Ind. Eng. Chem. (Anal. Ed.) **4**, 246 (1932); C. A. 2936 (1932).
[8] J. Meyerfeld, Chem.-Ztg. **34**, 948 (1910); C. A. 3178 (1910).

Exercise. Practice Analysis of a Mixture Containing Iron, Manganese, Aluminum and Chromium.—Make up a mixture containing Fe^{+++}, Mn^{++}, Al^{+++} and Cr^{+++} ions such that approximately 1 mg. of each cation is present in a volume of not more than 1 cc. To accomplish this, place two drops of each of the " 10-mg. per cc. stock test solutions " in a centrifuge tube. The total volume of the mixture will be about ½ cc. Add NH_4OH dropwise until precipitates no longer form, then centrifuge the mixture. According to Group Experiment 11, the precipitates formed are $Fe(OH)_3$, $Mn(OH)_2$, $Al(OH)_3$ and $Cr(OH)_3$.

Pipet off and discard the supernatant liquid. To separate this mixture of hydroxides, the amphoteric nature of aluminum and chromium hydroxides is utilized. Basing the separation on Experiments 12 and 13, add a few drops of water and then NaOH and finally Na_2O_2 to the residue in the centrifuge tube. Iron remains as $Fe(OH)_3$, and manganese, if not already partially oxidized by atmospheric oxygen, is here oxidized to $MnO(OH)_2$. The $Al(OH)_3$ dissolves to form the meta-aluminate ion, AlO_2^-, and the $Cr(OH)_3$ becomes the $CrO_4^=$ ion. Separate the residue from the solution by centrifuging, reserving the solution for tests for aluminum and chromium.

To show the presence of iron and manganese in the residue, dissolve the residue in a few drops of dilute HCl. Using drop portions of the solution, carry out the Prussian blue, the sulfosalicylic acid and the thiocyanate reactions as tests for iron.

In another portion of the solution prove the presence of manganese by the sodium bismuthate reaction. Other tests for manganese described under the reactions of this metal may, of course, also be tried here.

The supernatant liquid, reserved from the separation of iron and manganese, contains the aluminum in the form of the AlO_2^- ion and the chromium in the form of the $CrO_4^=$ ion.

The aluminum may be identified in this solution by properly carrying out the tests described previously using either alizarin, alizarin-S or aluminon reagent.

The chromate ion can be shown either by precipitating $BaCrO_4$ or else by hydrogen peroxide in ether according to the procedures previously given.

DIAGRAMMATIC SCHEME OF SEPARATION OF GROUP III A

Precipitation and Separation of the Ions of Group III B

Experiment 15. Action of H_2S and Precipitation of Group III B.—Pass H_2S into the three tubes containing the complex ions of nickel, cobalt and zinc, and into four other tubes containing a few drops of test solutions, respectively, of Mn^{++}, Fe^{+++}, Cr^{+++} and Al^{+++} made ammoniacal with NH_4OH. Note that precipitates form in all the tubes. With nickel, cobalt, zinc and iron the sulfides are formed; with manganese, the sulfide first forms and then rapidly oxidizes on exposure to air to the hydrated form, $MnO(OH)_2$; with aluminum and chromium the hydroxides are produced, the sulfides of these metals being completely hydrolyzed.

These reactions can be shown by the following equations:

$$2Fe^{+++} + 3S^{=} = \underline{Fe_2S_3}$$

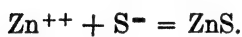
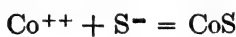
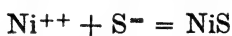
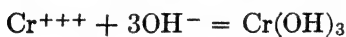
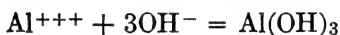
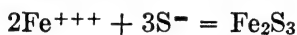
$$Mn^{++} + S^{=} = \underline{MnS} \rightarrow MnO(OH)_2$$

$$Al^{+++} + 3OH^{-} = \underline{Al(OH)_3}$$

$$Cr^{+++} + 3OH^{-} = \underline{Cr(OH)_3}$$

$$Ni^{++} + S^{=} = \underline{NiS}$$

$$Co^{++} + S^{=} = \underline{CoS}$$

$$Zn^{++} + S^{=} = \underline{ZnS}.$$

It should be noted that, whereas precipitates of sulfides or hydroxides are formed in all cases, the action of H_2S will be utilized in the scheme of analysis for this group only to precipitate NiS, CoS and ZnS from the ammoniacal solutions of their complex ions.

Experiment 16. Separation of Zinc from Nickel and Cobalt.—To the tubes containing NiS, CoS and ZnS add just enough concentrated HCl and a crystal of $KClO_3$ to dissolve the sulfides, and then add to each an excess of a strong solution of NaOH. The effect can be anticipated from the result of Experiment 12. $Ni(OH)_2$ and $Co(OH)_2$ precipitate and remain so in an excess of the reagent, whereas $Zn(OH)_2$, which first forms, dissolves to form soluble Na_2ZnO_2.

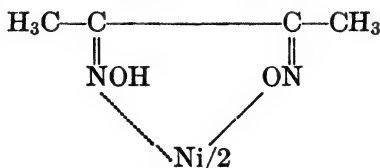
NICKEL, Ni^{++}

Nickel occurs commonly in the divalent condition. Anhydrous nickelous salts are, in general, yellow, but in solution and in the

hydrated form they are deep green. A trivalent form apparently exists in solution, but the salts are unstable and, with the possible exception of oxides and sulfides, no nickelic compounds are known in the solid state.

The behavior of nickel solutions toward alkalies and ammonium sulfide has already been considered. Nickel sulfide is peculiar in that it is not precipitated by H_2S from dilute HCl solution, and yet, after being precipitated from basic solution, it does not redissolve in dilute HCl and dissolves but slowly and with difficulty in the concentrated acid. This is explained by the existence of three forms of the sulfide, viz., α-, β- and γ-NiS.[1] α-NiS, the form first produced by H_2S, is soluble in very dilute acids ($0.01N$). Since no precipitate is obtained until the solubility product constant of α-NiS is exceeded, precipitation of nickel does not occur in Group II. However, after being precipitated, it rapidly polymerizes, forming β-NiS which is soluble in $2N$ HCl. This polymerizes still more, giving finally γ-NiS which is insoluble in acids unless oxidizing agents are present. NiS dissolves slightly in NH_4OH, forming a brown solution; however, some of the color may be due to colloidal NiS, which forms quite readily unless ammonium salts are present.

Tests for Nickel

α-Dimethylglyoxime (Diacetyl-Dioxime) Test.[2]—To a drop of nickel test solution on a spot plate add a drop of α-dimethylglyoxime, $H_3C—C(=NOH)—C(=NOH)—CH_3$ (printed as: $H_3C—C$———$C—CH_3$, with NOH and HON double-bonded below the two C atoms), solution and then make alkaline with dilute NH_4OH. A voluminous red precipitate of an inner complex compound is formed, its formula being:

Preliminary oxidation of the nickel by means of bromine water or sodium hypochlorite gives a more sensitive reaction. This reaction is often used to separate nickel from cobalt, and also for the gravimetric determination of nickel. Several other ions give

similar reactions (see under Copper, Iron, and Bismuth). The test is a specific example of a reaction which is characteristic of compounds containing the α-dioxime, —C————C, group[3]

$$\begin{array}{ccc} -\text{C} & \text{———} & \text{C}- \\ \| & & \| \\ \text{NOH} & & \text{HON} \end{array}$$

(the α-dioxime is that one of the three possible spatial isomers in which the two oxime groups are directed toward each other).

Other dioximes that have been proposed for the detection of nickel are α-diphenyl-dioxime (α-benzil-dioxime),[4] α-cyclohexane-dione-dioxime,[5] α-oxalene-diuramid-oxime[6] and α-furil-dioxime.[7] Of these, α-diphenyl-dioxime and α-furil-dioxime are claimed to give more sensitive tests than α-dimethylglyoxime.

Borax Bead Test.—In a loop of a platinum wire place some powdered borax, $Na_2B_4O_7 \cdot 10H_2O$, and heat in the flame. The mass first swells and then fuses into a clear bead of sodium metaborate, $NaBO_2$. Examine the bead to make sure it is colorless, then touch it to a small drop of a nickel test solution and heat in the outer oxidizing part of a hot flame. The bead turns brown, owing to the formation of nickel metaborate, $Ni(BO_2)_2$, or a double salt, $Na_2Ni(BO_2)_4$.

Supplementary Tests for Nickel

The above are the two most common confirmatory tests for nickel. Below are briefly described some other tests that have been proposed.

Rubeanic acid (dithio-oxal-diamide),[8] in alcoholic solution, gives a blue color with ammoniacal nickel solutions.

Nickel salts give a green precipitate with 8-hydroxy-quinoline.[9]

Ethylene-diamine, $(CH_2NH_2)_2$, added to a nickel solution and followed by a little sodium thiosulfate solution gives a violet crystalline precipitate of $[Ni\,en_2]S_2O_3$ (*en* represents the $(CH_2NH_2)_2$ molecule).[10] This test is the inverse of the nickel ethylene-diamine test for thiosulfates (q.v.).

A yellow color is obtained when oxamide, $(CONH_2)_2$, is added to a nickel solution and made alkaline with concentrated NaOH.[11]

Under the same conditions as in the preceding test, formaldoxime, $H_2C = NOH$, gives a brown color,[12] and nitro-amino-guanidine gives a blue color.[13] The latter is said to be a very sensitive test.

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COBALT, Co^{++}

Cobalt forms both a di- and a tri-valent series of salts, although the trivalent compounds, with the exception of double salts and complex compounds, are unstable and cannot be prepared in the solid form. The color of cobalt salts depends largely upon the degree of hydration, the hydrated salts being pink and the anhydrous blue.

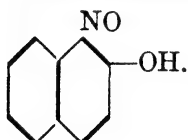
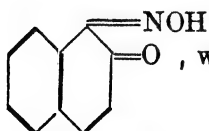
The formation of complex ions is an important property of cobalt, as it probably forms more complex compounds than any other metal. This property may be illustrated by the addition of NH_4OH to a cobalt solution. A greenish precipitate of a basic salt, e.g., $Co(OH)NO_3$, is first formed, but readily dissolves in an excess giving a reddish solution containing the $Co(NH_3)_6^{++}$ ion. This solution rapidly changes to a yellowish-brown color, due apparently to the formation of the cobaltic hexammine, $Co(NH_3)_6^{+++}$, ion by oxidation. Upon boiling, the color changes to purplish-red, caused by the entrance of an anion into the coordinated group, forming an ion of the type $[Co(NH_3)_5NO_3]^{++}$.

This complex-ion-forming property is further illustrated by the addition of concentrated HCl to a pink cobalt solution, whereupon the color changes to blue, owing apparently to the formation of the $CoCl_4^{=}$ ion, although it has also been explained as a dehydration effect. HBr and HI give even more pronounced colors than HCl, and these reactions have been used to detect cobalt.[1]

In connection with this behavior the familiar "sympathetic ink" experiment should be recalled, and it should also be noted that addition of excess alcohol to a concentrated aqueous cobalt solution will likewise produce the change to blue. The correct explanation probably is that in some cases it is complex-ion formation and in others dehydration.

The precipitation of cobalt sulfide by H_2S or $(NH_4)_2S$ has already been considered. CoS behaves toward acids in the same way as NiS, and for a similar reason.

Tests for Cobalt

α-Nitroso-β-Naphthol Test.[2]—To a drop of cobalt test solution on the white spot plate add a drop of a solution of the reagent,

A brownish-red precipitate of an inner complex salt with the formula is obtained. The reaction takes place with a tautomeric form of the reagent,

=NOH
=O , which is in equilibrium with the more familiar form.

This reaction may be used for the gravimetric determination of cobalt.

Because α-nitroso-β-naphthol has a relatively low solubility, similar, but more soluble, compounds have been proposed to increase the sensitivity of the test. Also, on account of this low solubility, a precipitate is sometimes obtained in the absence of cobalt, owing to dilution of the acetic acid solution of the reagent

and subsequent deposition of the reagent itself. β-Nitroso-α-naphthol is more sensitive than the other isomer.[3] Nitroso R salt (sodium 3,6 β-naphthol disulfonate), treated with HNO_3, gives with Co^{++} a beautiful red dye.[4] Other sulfonic acids have also been tried.[5]

Borax Bead Test.—Make a borax bead as described under Nickel, touch it to a cobalt test solution and then heat in the oxidizing flame. A blue color appears; it may be so intense as to render the bead opaque if much cobalt is present. If such is the case, dilute the solution or be careful to take up less solution on the bead. When cobalt and nickel are present together the cobalt masks the nickel color if the ratio of nickel to cobalt is less than about 33 to 1. At or near this ratio the bead is colorless, and with a higher proportion (50 to 1) of nickel the brown color is visible. As in the case of nickel, the color is due to the formation of a metaborate, $Co(BO_2)_2$, or a double salt, $Na_2Co(BO_2)_4$.

Thiocyanate (Vogel's) Tests.[6]—These tests are modifications of the same reaction; the simplest form is as follows:

Place a drop of cobalt test solution on a spot plate and add to it three drops of alcohol or, better, acetone. Drop in a crystal of NH_4CNS or add a drop of a saturated solution of NH_4CNS in acetone. A blue color, which becomes pink upon diluting with water, appears as a result of the formation of the $Co(CNS)_4^{=}$ ion.

The test as described above works in the absence of interfering ions. If ferric iron is present a red color is obtained, but this interference may be removed by reducing the iron to the ferrous state or by adding a fluoride, which removes it by forming the $FeF_6^{\equiv}$ ion. The effect of all interference may be overcome as follows: Place a crystal of NH_4CNS on a piece of spot paper and moisten with a drop of the solution to be tested. Develop with NH_3 until the spot is decolorized. A green spot may remain if Cr^{+++} is present, but any other color, such as red due to Fe^{+++}, will disappear. Dry the paper over a flame almost to the point of carbonizing the paper. A blue or bluish-green color (not the same as the spot before heating) now becomes apparent if cobalt is present. This modification is not as sensitive as the simple form first described.

The use of potassium cyanate, KCNO, instead of NH_4CNS in the above tests is said to increase the sensitivity.[7]

The inverse of the double thiocyanate test for mercury (q.v.)

may also be used to detect cobalt. A drop of test solution is placed on a glass slide and gently warmed; then a drop of the double thiocyanate, $Hg(CNS)_2 \cdot 2NH_4CNS$, solution is added. A blue precipitate of $Co(CNS)_2 \cdot Hg(CNS)_2$ is obtained.

Additional Tests for Cobalt

Double Nitrite Test.—Add a drop of dilute acetic acid to a drop of cobalt test solution on a spot plate and stir in solid KCl until the solution is saturated. Then add a drop of saturated KNO_2 solution. A yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$, results. The test is specific for cobalt, but if strongly colored ions are present it is difficult to observe the precipitate. Cesium nitrite (a mixture of $NaNO_2$ and $CsNO_3$ may be used) has been substituted for KNO_2, and it is claimed that the precipitate, $Cs_2NaCo(NO_2)_6$, forms more quickly and is less soluble than the corresponding potassium compound.[8]

Bicarbonate-Peroxide Test.[9]—To a drop of cobalt test solution on a spot plate add two or three drops of 3 per cent H_2O_2 and then drop in a crystal of potassium bicarbonate. A green color appears on the crystal; the compound formed is probably $CoCO_3 \cdot CoCoO_3$ or $[Co(KCO_3)_2]_2O$.

Rubeanic acid[10] (see also under Nickel) gives a brown precipitate with ammoniacal solutions of cobalt salts.

The addition of sodium thiosulfate, $Na_2S_2O_3$, to a cobalt salt, giving a blue color due to the formation of a thiosulfate analogous to the thiocyanate, is a sensitive test for this metal.[11]

When benzidine and dimethylglyoxime are added together to a neutral solution of a cobalt salt, an orange-red coloration results.[12] Cobalt and dimethylglyoxime alone give a brown color, but when ammonium sulfide is added a violet color appears.[13]

The action of Na_2O_2 or H_2O_2 on an ammoniacal cobalt solution produces a red color, due to a soluble cobalti-ammine.[14] Potassium ferrocyanide and ferricyanide produce red colors,[15] and sodium hyposulfite, $Na_2S_2O_4$,[16] and sodium bisulfite, $NaHSO_3$,[17] produce brown colors when added to ammoniacal cobalt solutions.

2,4-Dinitroso-resorcinol gives a deep red color with acidic cobalt solutions.[18]

When phenyl-thio-hydantoic acid is added to ammoniacal cobalt solutions a purplish-red precipitate results. This reaction is quantitative.[19]

Other tests involve the use of pyridine (Spacu reaction),[20] thioglycolic acid anilide,[21] antipyrine,[22] 8-hydroxyquinoline,[23] eriochrom blue-black B (G) and other dyes,[24] arseno-phosphotungstic acid[25] and many other substances.

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[17] Heinz, *loc. cit.*, reference 14.

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[19] H. H. Willard and D. Hall, J. Am. Chem. Soc. **44**, 2219 (1922); C. A. 3826 (1922).

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[21] T. Bersin, Z. anal. Chem. **85**, 428 (1931); C. A. 5865 (1931).
[22] K. Woynoff, Chem.-Ztg. **55**, 914 (1931); C. A. 1216 (1932).
[23] R. Berg, Z. anal. Chem. **76**, 191 (1929); C. A. 1588 (1929).
[24] E. Eegriwe, Z. anal. Chem. **82**, 150 (1930); C. A. 50 (1931).
[25] A. Lieberson, J. Am. Chem. Soc. **52**, 464 (1930); C. A. 1598 (1930).

ZINC, Zn^{++}

The two most important properties of zinc from the standpoint of methods of separation are: (1) its ability to form a complex ion with excess NH_4OH, a property which it shares with nickel and cobalt and which presents a method of separating these three elements from Fe, Mn, Al and Cr; and (2) its ability to form the zincate ion with NaOH, i.e., the amphoteric behavior of $Zn(OH)_2$, in this latter respect differing from nickel and cobalt and furnishing the means of separation of this element from the other two.

Tests for Zinc

The identification of zinc in the systematic scheme frequently gives trouble, not because of the lack of sensitive and satisfactory confirmatory reactions but because of failure to secure a satisfactory separation from the other ions of the group. Certain schemes of macro analysis base the final identification of zinc on the formation of the white sulfide; others rely on the ferrocyanide test or the formation of Rinmann's green.

Rinmann's Green Test.—Saturate a piece of filter paper with a solution of a zinc salt and add a very small amount of cobalt nitrate solution. Wrap the paper around a platinum wire or place it in a crucible and incinerate it until nothing but a light ash remains. This ash is colored a bright green by reason of the formation of cobalt zincate, $CoZnO_2$. If the ash remains black it indicates that too much cobalt was used. The test may also be carried out by using some long-fiber asbestos instead of the filter paper, in which way the interference of the carbon from the paper is avoided. Because of the difficulty of securing the correct cobalt concentration when the test is carried out as described, the test has been modified by Benedetti-Pichler by preparing test paper impregnated with a cobalti-cyanide solution. If these test papers are available place a drop of zinc solution on a square of this paper and incinerate it, obtaining thereby the green color more easily.[1]

Ferricyanide Tests.—Potassium ferricyanide, $K_3Fe(CN)_6$, when added to a zinc salt solution, forms a yellow or brown precipitate of zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$. This reaction has been modified and made more sensitive by the use of organic reagents.

If diethyl-aniline in H_2SO_4 solution is mixed with $K_3Fe(CN)_6$ solution and a drop of zinc solution is added, the ferricyanide is reduced to ferrocyanide and deeply colored oxidation products of the diethyl-aniline are formed. These are adsorbed by the zinc ferrocyanide, forming a red precipitate or color. The dye Orange IV[2] (Tropeolin OO) when mixed with $K_3Fe(CN)_6$ and made acidic gives a green precipitate when zinc is added. This test seems to be more satisfactory than that with diethyl-aniline. Metanil yellow may also be used in the same way. Diphenylamine,[3] C_6H_5–HN–C_6H_5, in glacial acetic acid solution gives a green precipitate when used in place of diethyl-aniline. The test with Orange IV is described in detail here and should be tried out with the zinc test solution.

Orange IV Test.—To a drop of Orange IV acidified with a drop of dilute H_2SO_4(1 : 24) reagent solution in a test tube add three to five drops of a 2 per cent solution of $K_3Fe(CN)_6$, the latter reagent freshly prepared within one week. A red color should be produced. Then add a drop of the zinc solution. A green coloration indicates the presence of zinc.

Other Tests for Zinc

If to a drop of zinc solution is added a very slight trace of copper and then a drop of a mixture of solutions of NH_4CNS and $Hg(CNS)_2$, an indigo color appears, due to the formation of $Zn(CNS)_2 \cdot Hg(CNS)_2$. The copper salt serves merely as a catalyst, and if more than a trace is present the color will be black instead of indigo.[4]

An alcoholic solution of resorcinol gives with Zn^{++} solutions a yellow color which becomes olive green or blue upon heating.[5]

Fischer[6] has found that diphenyl-thio-carbazone in CS_2 solution gives a purplish-red color which is concentrated in the CS_2 layer.

Pyridine in the presence of KCNS gives a white crystalline pre-

cipitate. This is said to be one of the most sensitive tests for zinc.[7] Antipyrine and pyramidon give analogous reactions.[8]

[1] A. Benedetti-Pichler, Ind. Eng. Chem., Anal Ed. **4**, 284 (1932); C. A. 4273 (1932).
[2] E. Eegriwe, Z. anal. Chem. **74**, 225 (1928); C. A. 3859 (1928).
[3] W. Cone and L. Cady, J. Am. Chem. Soc. **49**, 2214 (1927); C. A. 3581 (1927).
[4] F. Feigl and R. Stern, Z. anal. Chem. **60**, 1 (1921); C. A. 2598 (1921).
[5] P. Agostini, Ann. chim. applicata **19**, 164 (1929); C. A. 5430 (1929).
[6] H. Fischer, Mikrochemie [N. S.] **2**, 319 (1930); C. A. 893 (1931).
[7] R. Ripan, Bul. soc. stiinte Cluj **3**, 176 (1926); C. A. 1740 (1928).
[8] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4644 (1929).

Exercise. Practice Analysis of a Mixture Containing Nickel, Cobalt and Zinc.—Take two drops of each of the stock test solutions and place the mixture in a centrifuge tube. This mixture contains 1 mg. each of Ni^{++}, Co^{++} and Zn^{++} ion. Add dilute NH_4OH until the precipitates which are observed to form at first completely dissolve with the formation of $Ni(NH_3)_4{}^{++}$, $Co(NH_3)_6{}^{+++}$ and $Zn(NH_3)_4{}^{++}$. Pass H_2S into the mixture of complex ions. Centrifuge, and pipet off and discard the supernatant liquid.

Dissolve this mixture of sulfides by adding a crystal of $KClO_3$ and a few drops of concentrated HCl. Boil until free chlorine is no longer evolved, centrifuge if necessary and neutralize with NH_4OH.

In one portion show that nickel is present by the dimethylglyoxime reaction and in another portion demonstrate the presence of cobalt by the α-nitroso-β-naphthol reaction.

In order to separate zinc from nickel and cobalt use the amphoteric property of zinc hydroxide referred to in Experiment 16. Zinc may then be shown to be present by the cobalti-cyanide test paper or by the Orange IV reaction.

DIAGRAMMATIC SCHEME OF SEPARATION OF GROUP III B

Solution contains:		*Solution:*		*Precipitate:*		*Residue:*		*Solution:*
Ni^{++}	NH_4OH (excess)	$Ni(NH_3)_4{}^{++}$	H_2S	NiS	Conc. HCl $KClO_3$ NaOH	$Ni(OH)_2$	HCl	Ni^{++}
Co^{++}		$Co(NH_3)_6{}^{+++}$		CoS		$Co(OH)_2$		Co^{++}
Zn^{++}		$Zn(NH_3)_4{}^{++}$		ZnS		*Solution:* $ZnO_2{}^{=}$		

GROUP IV. THE AMMONIUM CARBONATE GROUP

BARIUM, Ba^{++}
STRONTIUM, Sr^{++}
CALCIUM, Ca^{++}

The alkaline earth elements, barium, strontium and calcium, are very much alike in their general chemical properties and in their analytical reactions. Magnesium also resembles these three elements, but in the systematic scheme of analysis, magnesium is prevented from precipitating, so that this analytical group, Group IV, includes only the first three elements mentioned.

Group Precipitation and Separation

The members of this group are distinguished from the ions of the following group by the fact that they are precipitated as carbonates by $(NH_4)_2CO_3$ in the presence of NH_4Cl. All these elements belong to the same group of the periodic table and their properties and reactions are quite similar, making their analytical separation relatively difficult. Most of the common inorganic salts of these three elements are soluble in water, the notable exceptions being the carbonates, chromates, sulfates and oxalates. The usual schemes of analysis for this group depend on differences in the solubilities of these four types of salts. The appended table gives the solubility of each salt in milligrams per cubic centimeter and forms the basis of the following groups of experiments. Much recent work has been done on the methods of analysis of this group utilizing organic solvents; the effect of acetone on the alkaline earth nitrates is shown in one of the following experiments.

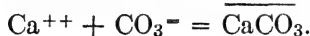
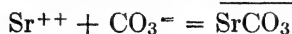
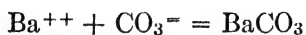
Solubilities of Alkaline Earth Salts

Milligrams per 1 cc. of Water

	Carbonate	Chromate	Sulfate	Oxalate
Barium	0.023	0.0038	0.0023	0.086
Strontium	0.011	1.20	0.11	0.046
Calcium	0.013	4.00	2.00	0.0056

Experiment 17. Action of $(NH_4)_2CO_3$.—On three glass slides or on the black spot plate place a drop each of Ba^{++}, Sr^{++} and

Ca^{++} test solution. To each add a drop of dilute NH_4OH. No precipitation of the alkaline earth hydroxides occurs, although a slight turbidity may form owing to traces of carbonates in the NH_4OH reagent. Now add to each a drop of $(NH_4)_2CO_3$ solution. White precipitates of $BaCO_3$, $SrCO_3$ and $CaCO_3$ are obtained. The reactions for this group precipitation are shown ionically by the equations:

$$Ba^{++} + CO_3^{=} = \underline{BaCO_3}$$
$$Sr^{++} + CO_3^{=} = \underline{SrCO_3}$$
$$Ca^{++} + CO_3^{=} = \underline{CaCO_3}.$$

Experiment 18. Action of K_2CrO_4.—Dissolve the precipitated carbonates by adding hot dilute acetic acid (it may be advantageous to transfer the mixtures to watch glasses), and add a drop of K_2CrO_4 solution. A precipitate of $BaCrO_4$ is readily obtained. Strontium chromate may also form but calcium chromate is too soluble to be precipitated.

Experiment 19. Action of H_2SO_4.—To single drops of the three ions add a drop of dilute H_2SO_4. White precipitates of $BaSO_4$, $SrSO_4$ and $CaSO_4$ are obtained, the order of increasing solubility being in the order named.

Experiment 20. Action of Ammonium Oxalate.—To drops of the three ions add a drop of dilute NH_4OH and then a drop of $(NH_4)_2C_2O_4$ solution. White precipitates of BaC_2O_4, SrC_2O_4 and CaC_2O_4 result. Try to dissolve the precipitates in hot acetic acid. BaC_2O_4 is completely soluble, SrC_2O_4 somewhat soluble and CaC_2O_4 practically insoluble.

Experiment 21. Action of Acetone on the Alkaline Earth Nitrates.—Crush a crystal of anhydrous $Ba(NO_3)_2$, place the powder in a micro test tube and add a few drops of acetone. Note that the salt is insoluble in this solvent. Repeat the experiment using $Sr(NO_3)_2$, and note that the effect is the same. Then place a crystal of $Ca(NO_3)_2 \cdot 4H_2O$ in a crucible and strongly heat it to render it anhydrous; transfer the dry powder to a test tube and add acetone. It will be found that the nitrate of calcium dissolves. This forms the basis of separating calcium from barium and strontium.

Experiment 22. Flame Tests.[1]—These are extremely import-

[1] Compare A. R. Clark, J. Chem. Education **12**, 242 (1935); C. A. **3623** (1935).

ant in identifying the ions of this group and should be carefully studied. Dip a clean platinum wire into a solution of a barium salt and hold in a Bunsen or Meker flame. Note the apple-green color which appears after a short time. Intensify the color by dipping the wire into concentrated HCl contained in a test tube and then replacing it in the flame. Repeat the dipping in HCl and heating several times. Then clean the wire by alternately dipping it in HCl and heating until it no longer colors the flame.

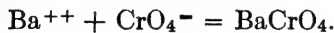
Repeat the procedure using a strontium compound. Strontium colors the flame a brilliant scarlet.

Repeat again using a calcium compound. Calcium gives a yellowish-red color to the flame. Then carry out the tests using the salts in pairs until the appearance of the flames due to the mixtures can clearly be distinguished.

BARIUM, Ba^{++}

As shown by the preceding experiments and the table of quantitative solubility of the common inorganic salts of the elements of this group, precipitation as carbonates offers the most feasible method of separation of the group as a whole. With respect to the separation of barium from strontium, the relatively great difference in the solubilities of $BaCrO_4$ and $SrCrO_4$ furnishes the best means of separation. According to Experiment 21, $Ba(NO_3)_2$ and $Sr(NO_3)_2$ are quite insoluble in acetone,[1] whereas $Ca(NO_3)_2$ is relatively soluble, and this circumstance is utilized in the separation of barium and strontium from calcium.

The commonly employed test for barium consists in the precipitation of yellow $BaCrO_4$:

$$Ba^{++} + CrO_4^{=} = \underline{BaCrO_4}.$$

Inasmuch as, under certain circumstances, strontium chromate may precipitate and lead to false indications the final identification is usually based on the green color of the flame. The flame spectrum of barium using a direct-vision hand spectroscope permits a more precise identification.

Sodium rhodizonate has been suggested as a test for barium by Feigl[2] and by Gutzeit,[3] the product having a red color. Strontium, however, interferes with this test, but calcium does not. Feigl[4] offers a method by which the strontium interference may

be overcome. The use of this reagent has not found much favor since its preparation is difficult and the reagent is itself quite unstable.

[1] P. Williams and H. Briscoe, Chem. News **145**, 177 (1932); C. A. 40 (1933).
[2] F. Feigl, Mikrochemie **2**, 188 (1924); C. A. 1108 (1925).
[3] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4644 (1929).
[4] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 255.

STRONTIUM, Sr^{++}

In the group separation, strontium is precipitated along with barium and calcium as the carbonate. The solubilities of the chromate and the sulfate lie between those of barium and calcium. The nitrate is quite insoluble in acetone, a property shared by barium nitrate.

The test recommended for strontium consists in the precipitation of $SrSO_4$, supplemented by the flame test.

CALCIUM, Ca^{++}

Comparing the solubilities in water of the common inorganic salts of calcium shows that the oxalate is by far the most insoluble. The reaction between $(NH_4)_2C_2O_4$ and Ca^{++} ion is therefore employed to isolate this element. To separate calcium from barium and strontium the method of Williams and Briscoe is recommended; this is based on the relatively greater solubility of $Ca(NO_3)_2$ in acetone.

Ammonium ferrocyanide[1] has been suggested as a test for calcium. The test is conducted by adding a drop of alcohol to a drop or two of test solution, and then solid NH_4Cl until nearly saturated, when a drop of $K_4Fe(CN)_6$ yields a white precipitate of calcium ferrocyanide.

Exercise. Practice Analysis of a Mixture Containing Barium, Strontium and Calcium.—Make up a mixture containing a few drops of each of the three test solutions. Make the solution basic with concentrated NH_4OH, and then add enough $(NH_4)_2CO_3$ to effect the complete precipitation of these ions as $BaCO_3$, $SrCO_3$ and $CaCO_3$. Centrifuge and then dissolve the carbonates in dilute HNO_3. Transfer the resulting solution to a

[1] F. Feigl and F. Pavelka, Mikrochemie **2**, 85 (1924); C. A. 797 (1925).

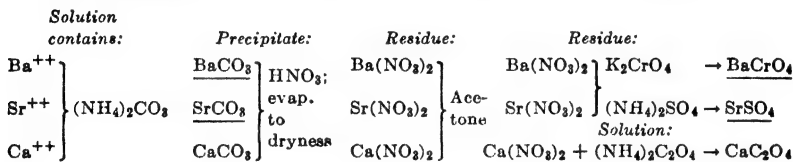
crucible and gently evaporate, being careful that spattering is avoided. Heat the dry residue in order to be sure that the nitrates are in the anhydrous form. Cool and powder the residue by crushing, and then add 1 cc. of acetone, with thorough stirring. After centrifuging, withdraw the supernatant liquid and use it for tests for calcium.

Dissolve the residue of $Ba(NO_3)_2$ and $Sr(NO_3)_3$, remaining from the calcium separation, in water; add a drop or two of dilute acetic acid and an equal quantity of ammonium acetate solution. Then heat and add dropwise enough dilute K_2CrO_4 reagent to effect the complete precipitation of the barium as $BaCrO_4$. Centrifuge the mixture, using the supernatant liquid for the test for strontium.

Strontium may best be tested for by adding $(NH_4)_2SO_4$, thus precipitating $SrSO_4$.

Confirm the presence of each element by flame tests, using a portion of the proper precipitate in making them.

DIAGRAMMATIC SCHEME OF SEPARATION OF GROUP IV

Solution contains:		*Precipitate:*		*Residue:*		*Residue:*		
Ba^{++}	$(NH_4)_2CO_3$	$BaCO_3$	HNO_3; evap. to dryness	$Ba(NO_3)_2$	Acetone	$Ba(NO_3)_2$	K_2CrO_4	$\rightarrow$ $BaCrO_4$
Sr^{++}		$SrCO_3$		$Sr(NO_3)_2$		$Sr(NO_3)_2$	$(NH_4)_2SO_4$	$\rightarrow$ $SrSO_4$
						Solution:		
Ca^{++}		$CaCO_3$		$Ca(NO_3)_2$		$Ca(NO_3)_2$	+ $(NH_4)_2C_2O_4$	$\rightarrow$ CaC_2O_4

GROUP V. THE SOLUBLE CATION GROUP

MAGNESIUM, Mg^{++}
AMMONIUM, NH_4^+
POTASSIUM, K^+
SODIUM, Na^+

This group consists of the ions that are not precipitated by the group reagents of the preceding four groups.

Experiment 23. Flame Tests.—Following the technique given in Group IV for flame tests, make flame tests of these four ions. Magnesium and ammonium give no color (except possibly a transient yellow due to unavoidable traces of sodium). Sodium gives a persistent yellow, and potassium a violet color. Try the test on a mixture of the two. Repeat, viewing the flame

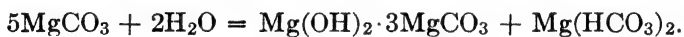
through a piece of cobalt glass. The glass absorbs the yellow color due to sodium and allows the violet color of the potassium flame to be seen.

MAGNESIUM, Mg^{++}

Most magnesium salts are white, and only a few are insoluble in water. In this latter respect magnesium resembles the alkali metals more closely than the alkaline earth metals of which periodic group it is a member.

Action of Hydroxides.—Ammonium hydroxide, or any soluble metal hydroxide, when added to a solution of a magnesium salt, produces a gelatinous precipitate of the sparingly soluble hydroxide, $Mg(OH)_2$. The presence of ammonium salts in sufficiently high concentration prevents the precipitation of $Mg(OH)_2$ by NH_4OH (common-ion effect). Magnesium hydroxide is soluble in water to the extent of 0.009 mg. per cc. at 18° C., but is readily dissolved by acids, even those as weak as carbonic.

Action of Carbonates.—From concentrated solutions of magnesium salts, soluble carbonates produce a white precipitate of magnesium carbonate, $MgCO_3 \cdot 3H_2O$. As with the hydroxide, no precipitate forms in the presence of ammonium salts. The crystalline precipitate apparently has no definite solubility in water but reacts with it with the formation of a basic carbonate of variable composition. Over a wide range of temperature this reaction with water is approximately expressed by the following equation (omitting water of hydration):

$$\underline{5MgCO_3} + 2H_2O = \underline{Mg(OH)_2 \cdot 3MgCO_3} + Mg(HCO_3)_2.$$

This basic carbonate is also precipitated from solutions too dilute to give a precipitate of the carbonate.

The above properties might be used in the separation of magnesium from the other metals but are not suitable for its identification; for this purpose the following tests are used.

Tests for Magnesium

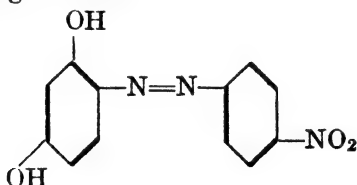
Phosphate Test.—Place a drop of magnesium test solution on a black spot plate or a glass slide and make ammoniacal with NH_4OH. Add solid NH_4Cl until the precipitate of $Mg(OH)_2$ disappears, and then add a drop of disodium hydrogen phosphate,

Na_2HPO_4, solution. A white precipitate of magnesium ammonium phosphate forms immediately or upon standing:

$$Mg^{++} + NH_4^{+} + PO_4^{\equiv} = \underline{MgNH_4PO_4}.$$

Although this is the least soluble inorganic salt of magnesium and is less soluble in NH_4OH than in water, complete (quantitative) precipitation occurs only after shaking and allowing to stand for some time because it readily forms a highly supersaturated solution.

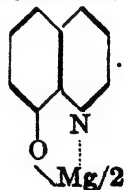
Under the same conditions an arsenate solution produces a precipitate of $MgNH_4AsO_4$ which resembles the phosphate very closely, but is somewhat more soluble.

***p*-Nitrobenzene-Azo-Resorcinol Test.**[1]—This reagent is a dye with the following formula:

It is also called *o*, *p*-dihydroxybenzene-azo-*p′*-nitrobenzene.

To a drop of magnesium test solution on a spot plate or in a test tube add two drops of the (alkaline) dye solution. The color changes from violet to a distinct blue, owing to adsorption of the dye on the surface of the precipitated $Mg(OH)_2$. Several other metals, notably cobalt and nickel, give similar colors, and the presence of ammonium salts, acetates and tartrates lowers the sensitivity of the test. Test papers for detecting magnesium with this reagent have been described.[2]

Feigl[3] suggests the use of *p*-nitrobenzene-azo-α-naphthol in place of the above reagent. One advantage claimed is that it is more sensitive.

8-Hydroxyquinoline ("Oxine") Test.[4]—Place a drop of magnesium test solution on a spot plate, saturate with solid NH_4Cl and add a drop of an alkaline solution of 8-hydroxyquinoline, . A greenish-yellow precipitate is obtained:

.

This compound is less soluble than $MgNH_4PO_4$ and has been applied to the quantitative determination of magnesium. Many other metals give similar precipitates.

Further Reactions of Magnesium

Many other tests for magnesium have been described, of which the following may be mentioned:

Quinalizarin Test.[5] — If a drop of quinalizarin (1, 2, 5, 8-tetrahydroxy-anthraquinone) is added to a solution containing magnesium, and 2*N* NaOH is added in excess, a blue precipitate is formed.

Titan Yellow (Acridine Yellow 5G) Test.[6]—If an aqueous solution of this reagent is added to a drop of a magnesium salt solution and made alkaline with NaOH, the color changes from a yellow brown to a fire red. A number of other dyes such as Clayton yellow, Congo corinth, dehydrothio-*p*-toluidine sulfonic acid[7] and aniline yellow also give color changes when used in the same way. Eegriwe[8] gives a list of at least six dyes which may be used to test for magnesium.

***p*-Phenylene-Diamine Test.**[9]—An aqueous solution of this reagent added to a magnesium salt solution and made alkaline with concentrated KOH gives a reddish-violet precipitate.

Diphenyl-Carbazide Test.[10]—An alkaline (NH_4OH) alcoholic solution of this reagent gives an insoluble red precipitate in the presence of magnesium.

Thio-diphenyl-carbazide gives a pink color.[11]

Iodine Test.[12]—Magnesium hydroxide also adsorbs iodine. If a drop of magnesium salt solution is mixed with a drop of a solution of iodine in potassium iodide and KOH is added, the precipitated $Mg(OH)_2$ is colored dark brown. Addition of more KOH removes the color from the solution surrounding the precipitate by converting the iodine to iodide and hypoiodite, and allows the precipitate to be seen as brown spots floating in a yellowish solution.

Silver Nitrate Test.[13]—If $Mg(OH)_2$ is precipitated on drop-reaction paper by adding NH_4OH to a drop of magnesium test solution, excess NH_3 being removed by warming, the addition of silver nitrate to the spot will give a brown precipitate of Ag_2O. If $HgCl_2$ is used instead of $AgNO_3$ the spot will be yellow.

Phenolphthalein Test.[13]—Phenolphthalein indicator solution added to a drop of neutral magnesium test solution, free from

ammonium salts, on drop-reaction paper gives a red color which disappears upon drying and reappears when the paper is moistened.

[1] J. Dubský and A. Okáč, Chem. Listy **24**, 492–3 (1930); C. A. 2660 (1931). L. Newell, N. Pike and J. Ficklen, Z. anorg. allgem. Chem. **225**, 281 (1935); C. A. 1322 (1936).

[2] I. Stone, Science **72**, 322 (1930); C. A. 5665 (1930).

[3] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 262.

[4] F. Hahn, Z. anal. Chem. **86**, 153–7 (1931); C. A. 5868 (1931).

[5] F. Hahn, Mikrochemie, Pregl Festschr. 127–39 (1929); C. A. 2397 (1930).

[6] I. M. Kolthoff, Mikrochemie, Emich Festschr. **1930**, 180; C. A. 3267 (1931).

[7] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4644 (1929).

[8] E. Eegriwe, Z. anal. Chem. **76**, 354–9 (1929); C. A. 2903 (1929).

[9] L. La Rosa, Ann. chim. applicata **22**, 725–8 (1932); C. A. 1840 (1933).

[10] F. Feigl, Mikrochemie **2**, 186–8 (1924); C. A. 1108 (1925).

[11] P. Agostini, Ann. chim. applicata **20**, 235 (1930); C. A. 5254 (1930).

[12] S. Augusti, Ann. chim. applicata **23**, 348 (1933); C. A. 5676 (1933).

[13] N. A. Tananaev, Z. anal. Chem. **88**, 93–4 (1932); C. A. 3454 (1932).

AMMONIUM, NH_4^+

Nearly all ammonium salts are soluble to a considerable extent in water, the important exceptions being noted below. The hydroxide, chloride, nitrate and acetate are important analytical reagents. The hydroxide, made by dissolving NH_3 in H_2O, in accordance with the reaction:

$$NH_3 + HOH = NH_4OH,$$

is a weakly ionized base, and contains in addition to NH_4^+ ions and OH^- ions some dissolved NH_3 as well as non-ionized NH_4OH. The equilibrium between the components in an aqueous solution of ammonium hydroxide is expressed by the relation:

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH} + C_{NH_3}} = K.$$

If a solution containing ammonium salts is treated with a strong base such as NaOH, this equilibrium is disturbed and ammonia is evolved from the mixture. This behavior is utilized in a number of the identifying tests for the NH_4^+ radical.

Ammonium salts are readily volatilized by heat. This prop-

erty is resorted to in removing ammonium salts from mixtures with other compounds.

In the solubility of its salts, the ammonium ion closely resembles that of potassium. The insoluble salts, which are like the corresponding potassium salts, are the yellow chloroplatinate, $(NH_4)_2PtCl_6$; the yellow cobaltinitrite, $(NH_4)_3Co(NO_2)_6$; the white acid tartrate, $NH_4HC_4H_4O_6$, and the white perchlorate, NH_4ClO_4. Consequently these precipitation reactions cannot be applied as identifying tests for the ammonium ion in the presence of potassium.

Tests for the Ammonium Ion

The tests for the presence of ammonium salts depend, as already stated, upon the displacement of NH_3 by treatment of the solution with NaOH. The test therefore resolves itself into showing the presence of NH_3 in the evolved gas. A number of sensitive tests for NH_3 are available. These are carried out in the following manner.

Odor and Litmus Paper Test.—Place two drops of NH_4NO_3 test solution in a small test tube, add an excess of strong NaOH solution and warm. Cautiously smell the gas issuing from the tube. The characteristic odor of NH_3 will probably be detected. It is more conclusive to insert a stopper containing a small funnel, thus completing the gas-evolution apparatus, and depend on the following chemical test. Moisten a piece of red litmus paper and place it in the funnel. The evolved NH_3 causes it to turn blue.

Test with Nessler's Reagent.—Nessler's reagent consists of a solution of $HgCl_2$ in KI. These two salts react to produce potassium mercuric iodide, K_2HgI_4, and in an excess of KOH react with NH_4OH to produce a brown precipitate:

$$2K_2HgI_4 + 3KOH + NH_4OH = \underline{NHg_2I} + 7KI + 4H_2O.$$

This extremely delicate test has been modified by Emich[1] into a micro test. The test is conducted by dipping a strip of filter paper in Nessler's reagent and holding it in the fumes escaping from the evolution tube.

Tannic Acid Test.[2]—On a spot plate dissolve a little solid tannic acid in a drop of water and add a drop of $AgNO_3$. Saturate two bits of filter paper with the solution, and place one in the

funnel of the gas-evolution apparatus, keeping the other as a blank. NH_3 causes the paper in the funnel to turn brown or black. The paper slowly turns brown from exposure to the air, hence the blank must always be used.

Hematoxylin Test.—Still another color reaction test on test paper is the hematoxylin test, advocated by Gutzeit.[3] Moisten a bit of paper with an alcoholic solution of hematoxylin and place it in the funnel of the evolution tube. NH_3 causes the appearance of a red or bluish-red color.

Feigl[4] suggests the use of *p*-nitrodiazobenzene as a test for ammonia.

[1] F. Emich, Lehrbuch der Mikrochemie, p. 109.
[2] K. Makris, Z. anal. Chem. **81,** 212 (1930); C. A. 4731 (1930).
[3] G. Gutzeit, Helv. Chim. Acta **12,** 713 (1929); C. A. 4644 (1929).
[4] F. Feigl, Mikrochemie **7,** 12 (1929); C. A. 4421 (1929).

POTASSIUM, K^+

Potassium salts are, as a rule, very soluble in water. They are less easily decomposed by heat than the ammonium salts. Like the corresponding ammonium salts, the following are the important insoluble salts of potassium and are used as precipitation tests: the chloroplatinate, K_2PtCl_6; the cobaltinitrite, $K_2NaCo(NO_2)_6$; the acid tartrate, $KHC_4H_4O_6$, and the perchlorate, $KClO_4$. The chloroplatinate and the perchlorate are used in the quantitative determination of potassium. The flame test, already referred to, is extremely delicate.

Tests for Potassium

Chloroplatinate Test.[1]—The reagent is chloroplatinic acid, made by dissolving platinum in aqua regia. To a drop of the KNO_3 test solution add a drop of the reagent. The reaction is:

$$2KNO_3 + H_2PtCl_6 = \underline{K_2PtCl_6} + 2HNO_3.$$

Since $(NH_4)_2PtCl_6$ resembles this, the test is not specific unless used in the absence of ammonium salts. In a systematic analysis, however, the ammonium salts are removed by volatilization before this test is applied.

Cobaltinitrite Test.[2]—This is the inverse of one of the tests for cobalt. Place a drop of test solution on a glass slide and add a

small amount of finely powdered $Na_3Co(NO_2)_6$. A yellow precipitate of $K_2NaCo(NO_2)_6$ is obtained. The NH_4^+ ion also gives a corresponding yellow precipitate. The test may be made more sensitive by adding a drop of $AgNO_3$ solution to the test solution before adding the reagent, in which case the yellow precipitate has the constitution $K_2AgCo(NO_2)_6$.[3]

[1] F. Emich, Lehrbuch der Mikrochemie, p. 108.
[2] L. de Koninck, Bull. soc. belg. chim. **23**, 200 (1909); C. A. 1628 (1909).
[3] L. Burgess and O. Kamm, J. Am. Chem. Soc. **34**, 652 (1912); C. A. 2044 (1912).

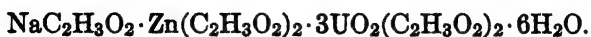
SODIUM, Na^+

All the ordinary salts of sodium are very soluble. The fluosilicate, Na_2SiF_6, and the pyroantimonate, $Na_2H_2Sb_2O_7$, are however, only slightly soluble in water and are sometimes used as precipitation tests for sodium. The uranyl acetate test, described below, is more satisfactory. The flame test is so delicate that traces of ever-present sodium compounds in reagents and the laboratory atmosphere will always tinge the flame a dull yellow. To show appreciable amounts of sodium the flame should show an intense persistent dandelion yellow color.

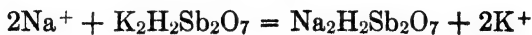
Tests for Sodium

Uranyl Acetate Test.—A number of metal uranyl acetates have been proposed as tests for sodium. Blanchetière[1] suggested, for the quantitative determination of sodium, a reagent prepared by mixing a solution of magnesium acetate in acetic acid with a solution of uranyl acetate in acetic acid, the mixed reagent when added to a solution containing sodium yielding a yellow precipitate of magnesium-uranyl-sodium acetate. This reagent was modified and suggested as a qualitative test for sodium by Kolthoff.[2] Later, Levy[3] working in Curtman's laboratory again modified the conditions in order to make the sodium test more specific.

The reagent recommended by Feigl[4] as a micro test is zinc uranyl acetate. This was proposed by Kolthoff[5] and has been favorably reported on by Emich,[6] Malitzkii and Tubakaiev,[7] Montequi and de Sábada[8] and others. The composition of the precipitated sodium compound is stated as

$$NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O.$$

Nickel uranyl acetate has been advocated by Feldstein and Ward.[9]

Pyroantimonate Test.—To a drop of test solution on a glass slide add a bit of solid KOH. Dissolve some $K_2H_2Sb_2O_7$ in an adjoining drop of water, and then mix the drops. A white precipitate of $Na_2H_2Sb_2O_7 \cdot 6H_2O$ is formed:

$$2Na^+ + K_2H_2Sb_2O_7 = \underline{Na_2H_2Sb_2O_7} + 2K^+$$

The solution must not be acid or the reverse would happen. Practically all ions interfere with this test.

[1] A. Blanchetière, Bull. soc. chim. **33**, 807–18 (1923); C. A. 3006 (1923).
[2] I. Kolthoff, Pharm. Weekblad **60**, 1251–5 (1923); C. A. 510 (1924).
[3] L. Curtman, Qualitative Chem. Analysis, pp. 250, 299, 334, 500 (1931).
[4] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 266.
[5] I. Kolthoff, Z. anal. Chem. **70**, 397 (1927); C. A. 1773 (1927).
[6] F. Emich, Lehrbuch, p. 108.
[7] U. Malitzkii and V. Tubakaiev, Mikrochemie **7**, 334–6 (1929); C. A. 3966 (1930).
[8] R. Montequi and R. de Sábada, Anales soc. españ. fís. quím. **29**, 255–61 (1931); C. A. 2938 (1931).
[9] P. Feldstein and A. Ward, Analyst **56**, 245 (1931); C. A. 3928 (1931).

EXERCISE. PRACTICE ANALYSIS OF A MIXTURE CONTAINING MAGNESIUM, AMMONIUM, POTASSIUM AND SODIUM.—Make up a mixture from the test solutions of these four cations. With drop portions of the mixture, and using the first three tests given under magnesium, show the presence of this element in the mixture.

Using the litmus paper test according to the previously described technique, demonstrate the presence of the ammonium ion in the mixture.

Transfer 6 or 8 drops of the mixture to a crucible, acidify with nitric acid and evaporate to dryness, baking the residue. Prove the presence of potassium in the residue by the cobaltinitrite test and the chloroplatinate test.

Conduct the zinc uranyl acetate test for sodium on a portion of the mixture.

PART III

THE REACTIONS OF THE ANIONS

The anions or acid radicals are the negatively charged ions resulting from the ionization of acids and salts. The anions included for study here are (1) the simple ions, i.e., negatively charged atoms, namely the iodide, I^-, bromide, Br^-, chloride, Cl^-, fluoride, F^-, and sulfide, $S^=$, ions; (2) the oxy-ions, namely the nitrite, NO_2^-, and nitrate, NO_3^-; the sulfate, $SO_4^=$, sulfite, $SO_3^=$, thiosulfate, $S_2O_3^=$; the chromate, $CrO_4^=$, and dichromate, $Cr_2O_7^=$; the arsenite, $AsO_3^{\equiv}$, arsenate, $AsO_4^{\equiv}$, phosphate, $PO_4^{\equiv}$, and borate, $BO_3^{\equiv}$; the carbonate, $CO_3^=$, oxalate, $C_2O_4^=$, tartrate, $C_4H_4O_6^=$, and acetate, $C_2H_3O_2^-$; silicate ions, of which the simplest is $SiO_3^=$; and (3) the nitrogen-containing anions, viz., the cyanide, CN^-; thiocyanate, CNS^-; ferricyanide, $Fe(CN)_6^{\equiv}$, and ferrocyanide, $Fe(CN)_6^{----}$.

In contrast to the systematic method of successive precipitation by which the cations are separated and subdivided into groups and subgroups and finally the individual cations freed from all others before identifying tests are applied, up to the present no such comparable scheme has been developed for the anions on the micro scale; in fact, even for the ordinary macro methods of analysis no entirely satisfactory method of separation has yet been proposed. Most of the anions must be tested for individually, in the presence of other anions. A definite order of applying tests, however, has been worked out, such that the interference of other anions is minimized. The order follows that in the senior author's *Elementary Qualitative Analysis.*

The anions considered in this manual have been classified into groups according to their behavior toward dilute HCl, a solution of a mixture of $BaCl_2$ and $CaCl_2$, and a nitric acid solution of $AgNO_3$. This grouping is made partly for the purpose for classifying the anions into groups and partly because, by a judicious use

of these group reagents, the presence or absence of groups as a whole may be shown and thus the labor of individual testing greatly reduced.

The Analytical Grouping of the Anions

The basis of the grouping will be evident from the following considerations.

1. If dilute HCl is added to separate portions of the individual salts or test solutions containing the anions, it will be found that the following are decomposed with the formation of gaseous products, viz., carbonates produce CO_2; sulfites and thiosulfates yield SO_2; nitrites on decomposition yield NO which oxidizes to brown fumes of NO_2; cyanides are decomposed and yield gaseous HCN; and some sulfides are dissolved with the formation of H_2S. These anions have therefore been classed together as Group I and called the Volatile Group.

2. If a solution of a mixture of $BaCl_2$ and $CaCl_2$ is added to separate portions of solutions of all the anions, the insoluble barium or calcium salts will be precipitated in the case of the following: carbonates, sulfites, arsenites, arsenates, phosphates, silicates, fluorides, chromates, sulfates, borates, oxalates and tartrates. Since, however, the first two are included in Group I, the remainder are considered as Group II and will hereafter be referred to as the $BaCl_2$-$CaCl_2$ Group.

3. If $AgNO_3$ is added to neutral solutions of all the anions, insoluble silver salts will be formed in all cases, with the exception of the fluoride, nitrate and acetate. But if the anion solutions are first acidified with dilute HNO_3 and the gaseous products removed and then the silver nitrate reagent added, precipitates will be formed only with the following: ferricyanides, ferrocyanides, thiocyanates, iodides, bromides and chlorides. In other words, the silver salts of these six anions are insoluble in nitric acid. This group of anions, Group III, called the $AgNO_3$–HNO_3 Group. therefore includes the above-mentioned anions.

4. Finally, the only anions not precipitated by either $BaCl_2$, $CaCl_2$ or $AgNO_3$, or decomposed into gases by dilute HCl, are the nitrate and acetate, and these are known as Group IV or the Soluble Group.

The grouping of the anions is summarized below:

Group I	*Group II*	*Group III*	*Group IV*
Nitrites	Arsenites	Ferricyanides	Nitrates
Cyanides	Arsenates	Ferrocyanides	Acetates
Sulfides	Phosphates	Thiocyanates	
Thiosulfates	Silicates	Iodides	
Sulfites	Fluorides	Bromides	
Carbonates	Chromates	Chlorides	
	Sulfates		
	Borates		
	Oxalates		
	Tartrates		

GROUP I. THE VOLATILE GROUP

NITRITES, NO_2^-
CYANIDES, CN^-
SULFIDES, $S^=$
THIOSULFATES, $S_2O_3^=$
SULFITES, $SO_3^=$
CARBONATES, $CO_3^=$

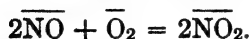
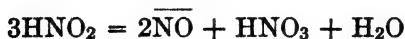
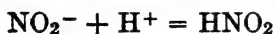
This group derives its name from the fact that, when dilute HCl is added to mixtures containing ions or salts of members of this group, gases are evolved. This property of the members of this group can be shown by the following experiment.

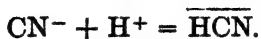
Experiment 24.—In six separate test tubes place a few crystals of the sodium salts of NO_2^-, CN^-, $S^=$, $SO_3^=$, $S_2O_3^=$ and $CO_3^=$. To each tube add a drop or two of dilute HCl. Note the evolution of a gas in each case.

In the case of the nitrite, observe the evolution of a brown gas, NO_2, formed from NO by atmospheric oxidation. The reactions taking place are shown by the equations:

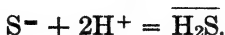
$$NO_2^- + H^+ = HNO_2$$

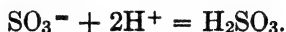
$$3HNO_2 = 2\overline{NO} + HNO_3 + H_2O$$

$$2\overline{NO} + \overline{O}_2 = 2\overline{NO}_2.$$

The NaCN when treated with HCl yields gaseous HCN:

$$CN^- + H^+ = \overline{HCN}.$$

Very cautiously note its odor.

Sulfides when acted upon by HCl evolve hydrogen sulfide, a gas whose properties and odor have already become familiar:

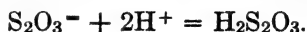
$$S^{=} + 2H^{+} = \overline{H_2S}.$$

Sulfites when acidified yield the unstable sulfurous acid:

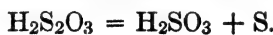
$$SO_3^{=} + 2H^{+} = H_2SO_3.$$

This decomposes into SO_2 and H_2O:

$$H_2SO_3 = \overline{SO_2} + H_2O.$$

Note the odor of sulfur dioxide, that of burning sulfur.

The action of HCl on $Na_2S_2O_3$ is first to form thiosulfuric acid:

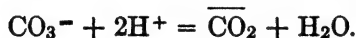
$$S_2O_3^{=} + 2H^{+} = H_2S_2O_3.$$

This is unstable and decomposes into H_2SO_3 and free sulfur:

$$H_2S_2O_3 = H_2SO_3 + \underline{S}.$$

The sulfurous acid further decomposes into SO_2 and water:

$$H_2SO_3 = \overline{SO_2} + H_2O.$$

It should be remembered that both sulfites and thiosulfates yield SO_2, but with the thiosulfate a voluminous residue of yellow sulfur remains.

The Na_2CO_3 is decomposed by the hydrochloric acid, giving first carbonic acid, which further decomposes into carbon dioxide and water:

$$CO_3^{=} + 2H^{+} = \overline{CO_2} + H_2O.$$

Properties and Tests

NITRITES, NO_2^-

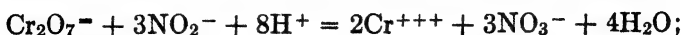
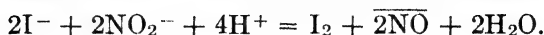
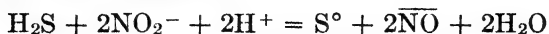
All normal nitrites are soluble in water (silver nitrite, however, is only slightly soluble) but some complex nitrites, such as $K_3Co(NO_2)_6$, are quite insoluble. Nitrites may act either as reducing agents or as oxidizing agents; the following equations illustrate these two actions, as a reducing agent:

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{++} + 5NO_3^- + 3H_2O$$

$$Cr_2O_7^{=} + 3NO_2^- + 8H^+ = 2Cr^{+++} + 3NO_3^- + 4H_2O;$$

and as an oxidizing agent:

$$H_2S + 2NO_2^- + 2H^+ = S^\circ + 2\overline{NO} + 2H_2O$$

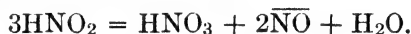
$$2I^- + 2NO_2^- + 4H^+ = I_2 + 2\overline{NO} + 2H_2O.$$

Although NO is the usual product of reduction, it is possible for lower reduction products, e.g., N_2O, N_2 or NH_3, to be formed in particular cases.

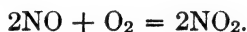
Nitrites may be formed from nitrates by heating:

$$2KNO_3 = 2KNO_2 + \overline{O}_2.$$

Reducing agents may produce the same effect.

Nitrous acid, HNO_2, is liberated from its salt by treatment with stronger acids. The free acid readily decomposes, liberating nitric oxide and forming nitric acid:

$$3HNO_2 = HNO_3 + 2\overline{NO} + H_2O.$$

Because of this reaction it is difficult to obtain a nitrite solution that does not contain at least a small amount of nitrate. The colorless NO readily oxidizes in the air, forming brown fumes of nitrogen dioxide, NO_2:

$$2NO + O_2 = 2NO_2.$$

Tests for Nitrites

Starch-Potassium Iodide Test.—Add a few drops of dilute HCl to a few particles of $NaNO_2$ contained in a test tube, warm gently and hold in the escaping gas a strip of moistened starch-potassium iodide paper. The NO_2 oxidizes the KI, liberating I_2, which forms an intense blue adsorption complex with the starch. Dipping the paper into an acidified nitrite solution makes possible the detection of smaller amounts of nitrite (1 : 10,000,000), but there is obviously more chance for interference by oxidizing agents which liberate iodine in using this procedure.

Ferrous Sulfate Test.—Place a drop of test solution on a spot plate, acidify with dilute H_2SO_4 and drop in a crystal of $FeSO_4$. A brown or greenish-brown color appears around the crystal, due to the formation of nitrosyl ferrous sulfate, $Fe(NO)SO_4$. Nitrates give a similar result, but by the substitution of acetic acid for the H_2SO_4 the color appears only in the case of nitrites. Iodides, bromides, colored ions and anions that give colored compounds with ferrous salts must be absent.

Diphenyl-Amine Test.[1]—Dissolve a few crystals of diphenylamine, $C_6H_5—NH—C_6H_5$, in concentrated H_2SO_4 on a spot plate. Take up a drop of the reagent in the loop of a platinum wire and hold it in the escaping gas from a warm, acidified nitrite solution. The drop is colored an intense blue.

This reaction may also be carried out by adding the diphenylamine reagent to the nitrite solution, in the absence of nitrates and other oxidizing agents.

Additional Reactions of Nitrites

Diazo Reactions (Griess).—By the action of HNO_2 on aromatic amines the so-called diazo compounds are formed. If these compounds are " coupled " with suitable compounds intensely colored dyes result. Since diazo compounds are formed only by HNO_2, such a series of reactions may be used to detect this acid. Several pairs of amines and couplers have been proposed:

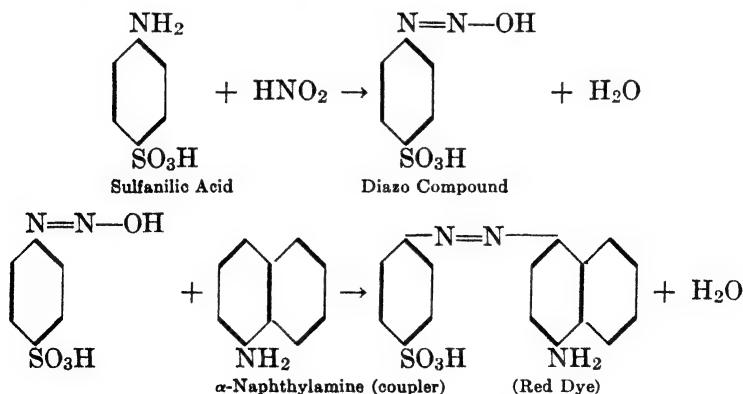
Sulfanilic Acid-α-Naphthylamine.[2]—To a drop of test solution acidified with acetic acid add a drop of sulfanilic acid solution and then a drop of α-naphthylamine solution. A red color forms immediately or after a short time.

The α-naphthylamine solution must be colorless before conducting the test (the appearance of a color indicates partial decomposition and this colored reagent will sometimes give a color with sulfanilic acid alone). The reactions are as follows:

$$NH_2—C_6H_4—SO_3H + HNO_2 \rightarrow (N{=}N—OH)—C_6H_4—SO_3H + H_2O$$

Sulfanilic Acid — Diazo Compound

$$(N{=}N—OH)—C_6H_4—SO_3H + C_{10}H_7NH_2 \rightarrow HO_3S—C_6H_4—N{=}N—C_{10}H_6—NH_2 + H_2O$$

α-Naphthylamine (coupler) — (Red Dye)

The test may also be carried out with paper impregnated with the two reagents.[3]

A similar test can be made by adding to a drop of test solution on a spot plate a drop of a saturated acetic acid solution of benzidine.[4] A red color appears. When a drop of an alcoholic solution of β-naphthol and one of NH_4OH are added the red color changes to violet. The reactions are similar to those above.

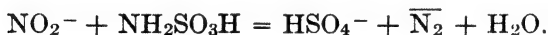
Many other combinations of amines and couplers have been investigated. Fuchsine, or magenta, with β-naphthol or α-naphthylamine as coupler has been recommended as the most sensitive test.[5] Safranine-T[6] dissolved in H_2SO_4 gives a blue color with nitrites.

Antipyrine[7] added to a nitrite solution and made acid with H_2SO_4 gives a green color. Many cations interfere, but the test may be used in the presence of nitrates.

If a nitrite solution is acidified with acetic acid and a little apomorphine is added, the solution, after heating to boiling, cooling and shaking with ethyl acetate, assumes a violet color.[8] Many other substances (oxidizing agents) give the same test, but nitrates do not.

An acetic acid solution of benzidine added to a nitrite solution on spot paper gives a deep red to yellow-pink coloration.[9] Chromates interfere but may be removed by precipitating with $BaCl_2$.

Amino-sulfonic acid[10] reacts with nitrites, liberating bubbles of nitrogen and forming a sulfate, and the formation of either of these products may be used to detect nitrites (the latter only if sulfates are first removed with $BaCl_2$). The reaction is quantitative:

$$NO_2^- + NH_2SO_3H = HSO_4^- + \overline{N_2} + H_2O.$$

An acidified nitrite solution added to an aqueous solution of walnut kernels gives a flame-red coloration which turns violet and finally becomes blue or yellow.[11] The reaction is due to a tannin in the walnut kernels.

A very dilute, practically colorless, solution of potassium ferrocyanide acidified with acetic acid is colored greenish-yellow when a nitrite is added. Nitrates do not interfere.

A red color is obtained when a nitrite is added to a solution of resorcinol in concentrated H_2SO_4.[12]

When acetic acid, potassium oxalate, manganous sulfate and hydrogen peroxide are added, in the order given, to a nitrite solution, a red color is obtained.[13]

Urea, $CO(NH_2)_2$, added to a nitrite acidified with HCl evolves

nitrogen, bubbles of which can be seen forming in the liquid. Sodium azide, NaN_3, also liberates nitrogen by its action with a nitrite.[14]

[1] F. Hahn, Mikrochemie, Emich Festschr. **1930**, 143; C. A. 3272 (1931).
[2] J. Blom, Ber. **59**, 121 (1926); C. A. 1368 (1926).
[3] F. Hahn, Mikrochemie **3**, 31 (1931); C. A. 1181 (1931).
[4] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).
[5] J. Dubský and A. Okáč, Z. anal. Chem. **75**, 92 (1928); C. A. 63 (1929).
[6] E. Eegriwe, Z. anal. Chem. **69**, 382 (1926); C. A. 873 (1927).
[7] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).
[8] F. Pavelka, Mikrochemie **8**, 46 (1930); C. A. 1600 (1930).
[9] N. Ronzhina, J. Russ. Phys.-Chem. Soc. **61**, 897 (1929); C. A. 569 (1930).
[10] F. Hahn and P. Baumgarten, Ber. **63B**, 3028 (1930); C. A. 894 (1931).
[11] P. Zywnev, Z. anal. Chem. **79**, 389 (1930); C. A. 1821 (1930).
[12] T. Rodillon, J. pharm. chim. **26**, 376 (1922); **27**, 64 (1923); C. A. 1521 (1923).
[13] P. Hermans, Pharm. Weekblad **57**, 462 (1920); C. A. 3039 (1920).
[14] For additional tests see: G. Carpentier, Union pharm. **72**, 162 (1932); C. A. 5449 (1933). E. Migray, Chem.-Ztg. **57**, 94 (1933); C. A. 1592 (1933).

CYANIDES, CN^-

Cyanides and the free acid, HCN, are very poisonous and should be examined with care. All tests with materials known to contain or suspected of containing cyanides should be made with this caution in mind.

Cyanides readily form a large number of complex ions, as for example, the complex silver, copper and cadmium ions previously mentioned in the discussion of the properties of these metals and the ferrocyanides and ferricyanides to be discussed later. The ease with which these complex ions are formed often serves as a test for cyanides.

Acidification of a solution containing a cyanide results in the evolution of gaseous HCN which has a characteristic odor of bitter almonds (pure HCN is a liquid at room temperatures but is easily volatilized). HCN is such a weak acid that even carbonic acid can set it free, so that solid soluble cyanides always possess this odor when exposed to the air.

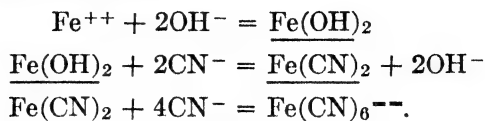
Tests for Cyanides

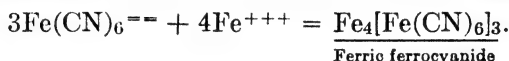
Prussian Blue Test.—To a sodium cyanide solution in a test tube add a drop of NaOH and then a drop of freshly prepared

$FeSO_4$ solution and heat to boiling. Ferrous cyanide, $Fe(CN)_2$, is formed but dissolves in an excess of the cyanide solution with the formation of a ferrocyanide:

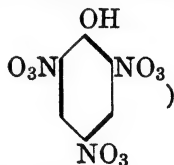
$$Fe^{++} + 2OH^- = \underline{Fe(OH)_2}$$

$$\underline{Fe(OH)_2} + 2CN^- = \underline{Fe(CN)_2} + 2OH^-$$

$$\underline{Fe(CN)_2} + 4CN^- = Fe(CN)_6^{----}.$$

Acidify the solution with HCl, and add a drop of $FeCl_3$ solution. A blue precipitate of ferric ferrocyanide (Prussian blue) forms:

$$3Fe(CN)_6^{----} + 4Fe^{+++} = \underset{\text{Ferric ferrocyanide}}{\underline{Fe_4[Fe(CN)_6]_3}}.$$

The test may also be performed by liberating the HCN with HCl and absorbing the evolved gas in NaOH on a piece of paper held in the mouth of the tube or in the funnel of the gas-evolution apparatus, then adding $FeSO_4$ and finally $FeCl_3$.

Decolorization Test.[1]—Moisten a strip of filter paper with ammoniacal copper nitrate solution and hold it in a stream of H_2S to precipitate CuS. Allow the paper to dry, and then place a drop of cyanide solution on it. The CuS is dissolved with the formation of $Cu(CN)_4^{\equiv}$, leaving a clear spot on the paper. The spot covered by the drop should be compared with the rest of the paper, which serves as a blank. Addition of NH_4OH to an unknown test solution will prevent the formation of precipitates if ferrocyanides, ferricyanides and thiocyanates are present.

Picric Acid Test.[2]—Dip a strip of filter paper into a saturated aqueous solution of picric acid (tri-nitro-phenol, [benzene ring with OH; O_3N, NO_3; NO_3]) then into a solution of Na_2CO_3. Add a drop of the cyanide solution and dry the paper. A red or red-brown color appears. Sulfides give a somewhat similar color.

If finely powdered $CuSO_4$ is mixed with ten times its weight of guaiacol (monomethyl ether of pyrocatechol) on a spot plate and a drop of cyanide solution added to this mixture, a red coloration is produced on the particles of $CuSO_4$.[3] Ferrocyanides and ferricyanides give similar colors, and a greenish-brown color results with thiocyanates.

Tincture of guaiac[3] added to a copper solution on spot paper is turned a deep blue color when dipped into a solution of a cyanide.

Evaporation of a cyanide with ammonium polysulfide until no more H_2S is evolved results in the formation of the thiocyanate ion, CNS^-, and addition of $FeCl_3$ to the resulting thiocyanate solution provides a very sensitive test for cyanides.

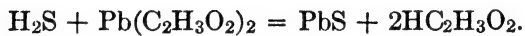
[1] O. Barnebey, J. Am. Chem. Soc. **36**, 1092 (1914); C. A. 2662 (1914).
[2] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).
[3] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

SULFIDES, $S^=$

The sulfides of most of the metals are insoluble in water, those of the alkaline earths and of the alkali metals, however, being soluble in water and easily hydrolyzed. Aluminum and chromium sulfides also hydrolyze. Nitric acid dissolves all sulfides with the exception of HgS. The free acid, H_2S, is a gas with a distinctive foul odor. The free acid as well as acidified solutions of sulfides are good reducing agents, reducing such oxidizing agents as $KMnO_4$ and chromates.

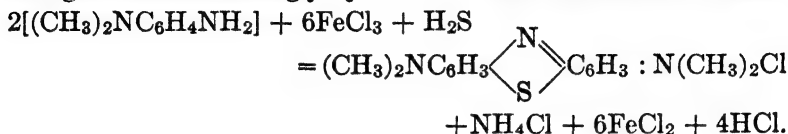
Tests for Sulfides

Lead Acetate Test.—Moisten a strip of filter paper with a solution of basic lead acetate or else use lead acetate test paper. Place a few drops of a sulfide solution in the evolution apparatus, add a drop of dilute HCl and hold the test paper over the funnel. The paper will turn brown or black owing to the precipitation of PbS on the paper, the reaction being:

$$H_2S + Pb(C_2H_3O_2)_2 = \underline{PbS} + 2HC_2H_3O_2.$$

Sodium Nitroprusside Reaction.—This reagent, $Na_2Fe(CN)_5NO$, reacts with alkaline sulfide solutions to give a violet-red color. Conduct the test as follows. To a few drops of the sulfide, rendered alkaline with a drop of NaOH, add a drop or two of a 1 per cent solution of the reagent. This test is very sensitive but is not given by H_2S.

Formation of Methylene Blue.[1]—Place a drop of test solution in a micro crucible. Place a drop of NaOH on a glass slide.

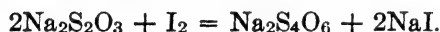
Add a drop of dilute HCl to the crucible, invert the glass slide over the crucible and gently heat the crucible. Then remove the slide and add a few crystals of *p*-amino-dimethylaniline, followed by a small drop of concentrated HCl and a drop of $FeCl_3$ solution. A reddish color changing to a blue will result. The color may be brought out more strongly by dilution of the mixture with water:

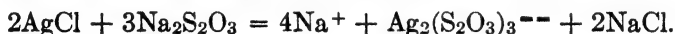
$$2[(CH_3)_2NC_6H_4NH_2] + 6FeCl_3 + H_2S$$
$$= (CH_3)_2NC_6H_3\langle{}^{N}_{S}\rangle C_6H_3 : N(CH_3)_2Cl$$
$$+ NH_4Cl + 6FeCl_2 + 4HCl.$$

This test is also given in a solution containing sulfides.

[1] W. Mecklenburg and F. Rosenkränzer, Z. anorg. allgem. Chem. **86**, 146 (1914); C. A. 1938 (1914).

THIOSULFATES, $S_2O_3^{=}$

The sodium salt, $Na_2S_2O_3$, is a very important analytical reagent, being a strong reducing agent. It reacts quantitatively with iodine, reducing it and becoming oxidized itself to sodium tetrathionate in accordance with the equation:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

$Na_2S_2O_3$ is the " hypo " of the photographer, and is used to dissolve the unreduced portions of silver salt in the photographic film. With silver chloride it forms a complex ion:

$$2AgCl + 3Na_2S_2O_3 = 4Na^+ + Ag_2(S_2O_3)_3^{----} + 2NaCl.$$

Hydrochloric acid reacts to form the free acid, thiosulfuric acid, $H_2S_2O_3$, which is unstable, decomposing into sulfur, SO_2 and H_2O:

$$S_2O_3^{=} + 2H^+ = H_2S_2O_3 = \overline{SO_2} + \underline{S} + H_2O.$$

The evolution of SO_2 accompanied by the precipitation of sulfur furnishes an indication of the presence of thiosulfates.

The sulfur di[illegible]evolved on treatment with dilute acids may be tested [illegible] the several methods given under sulfites.

Tests for Thiosulfates

Antimony Chloride Test.[1]—Place several drops of the test solution on a glass slide. Heat to boiling, and add a few grains

of $SbCl_3$. A vermilion color on the crystals of the salt shows the presence of thiosulfates. The presence of sulfites does not interfere with this test.

Sodium Azide Test.—If a drop of thiosulfate solution is placed in a micro crucible and sufficient very dilute iodide-starch solution (0.005 *N*) added to leave a blue color, and this followed by a drop of 2 per cent sodium azide, NaN_3, the color is discharged.[2]

Ethylenediamine is recommended by Spacu and Spacu[3] as a sensitive test for thiosulfates. The reagent is made by adding ethylenediamine to a solution of $Ni(NO_3)_2$ until a violet color develops. With a cold, neutral or slightly alkaline solution of $Na_2S_2O_3$ a violet precipitate forms.

[1] G. Gutzeit, Helv. Chim. Acta **12,** 713 (1929); C. A. 4645 (1929).

[2] E. E. Jelley and W. Clark, Brit. J. Phot. **76,** 714 (1929); C. A. 3967 (1930). Also F. Feigl, Z. anal. Chem. **74,** 369 (1928); C. A. 4083 (1928).

[3] G. Spacu and P. Spacu, Z. anal. Chem. **89,** 192 (1932); C. A. 5032 (1932).

SULFITES, $SO_3^{=}$

The alkali sulfites are soluble in water, most of the others being insoluble in water but soluble in acids. Na_2SO_3 and free sulfurous acid, H_2SO_3, are excellent reducing agents. H_2SO_3 is unstable and decomposes into SO_2 and water. SO_2 is liberated by treatment of a sulfite with a strong acid.

Tests for Sulfites

Barium Hydroxide Test for SO_2.—Treat a few drops of test solution with dilute HCl in the evolution apparatus, and hold in the escaping gas a drop of $Ba(OH)_2$ held in the loop of a platinum wire. The drop becomes turbid due to the precipitation of $BaSO_3$.

Tests made with drops of test solution are:

Nitroprusside Test.[1]—Place a few drops of a saturated solution of $ZnSO_4$ and a drop of $K_4Fe(CN)_6$ solution together with one or two drops of sodium nitroprusside on [illegible]ate. Then add a drop of test solution. A red color deve[illegible]ulfides interfere with this test (see the nitroprusside test fo[illegible]fides), but thiosulfates do not.

Another test with which thiosulfates do not interfere is the following: Place a drop of test solution on a glass slide; add a drop

of dilute $HC_2H_3O_2$ and then one of the reagent which is prepared by mixing 5 grams of $Cd(C_2H_3O_2)_2$ with 2.5 cc. of aniline, and diluting to 100 cc. A white precipitate forms.[2]

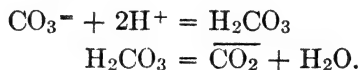
Fuchsin Test.[3]—This reagent is decolorized by very small amounts of sulfite, and thiosulfates do not interfere. The reagent is a very dilute, slightly acidified solution of fuchsin, and to it is added the solution of the sulfite, neutral to phenolphthalein.

Malachite green, like fuchsin, is decolorized by sulfites as well as by sulfides but not by thiosulfates or sulfates.[4]

[1] F. Feigl, Tüpfelreaktionen, 2nd edition, pp. 308–9.
[2] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).
[3] V. E. Malinovskii, Urainskii Khem. Zhurnal **5**, 181 (1930); C. A. 2076 (1931).
[4] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 311.

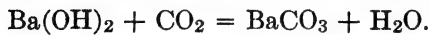
CARBONATES, $CO_3^{=}$

The carbonates of the alkali metals are soluble in water; all other carbonates are insoluble in water but dissolve in acids stronger than carbonic. All carbonates when treated with strong acids evolve CO_2, carbonic acid first forming and then decomposing according to the reactions:

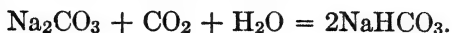
$$CO_3^{=} + 2H^+ = H_2CO_3$$
$$H_2CO_3 = \overline{CO_2} + H_2O.$$

A test for the presence of CO_2 constitutes a test for carbonates.

Tests for Carbonates

Barium Hydroxide Test for CO_2.—Treat a few drops of Na_2CO_3 with dilute HCl in a test tube. Hold over the mouth of the tube a drop of $Ba(OH)_2$ solution held in the loop of a platinum wire. The turbidity which forms in the drop is due to the formation of $BaCO_3$:

$$Ba(OH)_2 + CO_2 = \underline{BaCO_3} + H_2O.$$

It should be noted that SO_2 evolved by acidifying a sulfite or a thiosulfate will also render $Ba(OH)_2$ turbid. This interference is overcome, in systematic analysis, by first oxidizing the SO_2 with H_2O_2 or some other oxidizing agent, and thus making the test specific for carbonates.

Phenolphthalein Test.[1]—Carbon dioxide reacts with sodium carbonate to form sodium bicarbonate according to the reaction:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

Phenolphthalein, a substance used extensively as an indicator, is pink in Na_2CO_3 solution and colorless in $NaHCO_3$ solution. If, therefore, a drop of this substance is rendered alkaline by Na_2CO_3 and held in the loop of a platinum wire and exposed to CO_2, the color will fade. The indicator solution is prepared by mixing 2.5 cc. of a 0.5 per cent solution of phenolphthalein, 1 cc. of $0.1N$ Na_2CO_3 and 10 cc. of water.

H_2SO_3, H_2S and HCN interfere with this test since these acids will also decolorize the indicator. The interference from sulfites is overcome by the use of H_2O_2, and that from HCN and H_2S by $HgCl_2$.

EXERCISE. PRACTICE ANALYSIS OF A MIXTURE OF ANIONS OF GROUP I.—The sample may best be made by mixing the sodium salts, adding 1 cc. of water, heating the mixture and removing the solution with a pipet. Several such treatments with water should be given, the final combined solution being then diluted to a volume of 5 cc. with water. About 1 cc. of the mixture should be taken, from which drop portions are withdrawn for tests, the remainder being reserved for additional tests.

In conducting the tests, it should be borne in mind that this mixture consists of Group I anions only, and that certain of the tests, though conclusive when applied here, are not decisive when anions of other groups are present, as in the complete systematic analysis of materials of unknown composition. As shown in the preliminary experiments, some of the tests are made with the escaping gas and others are conducted in the solution.

The addition of HCl, in all the tests which are to be conducted in the gaseous phase, will evolve a gas mixture consisting of HCN, NO_2, H_2S, SO_2 and CO_2. Separately these gases have distinctive odors, with the exception of CO_2, and all are colorless except NO_2 which may be present in sufficient amount to give a brownish tinge. Not much reliance can be placed on color indications, however, for the absence of a brown color should not be taken as

[1] F. Feigl and P. Krumholz, Mikrochemie [N. S.] **2**, 131 (1930); C. A. 4238 (1930).

final evidence of the absence of nitrites. Nor can the odor be depended upon in this mixture of gases.

Furthermore, one gas may react with another before the proper tests can be applied. Thus SO_2 reacts with H_2S, in solution, according to the equation:

$$5H_2SO_3 + 5H_2S = \underline{5S} + H_2S_5O_6 + 9H_2O.$$

and nitrogen dioxide may oxidize one or another of the reducing gases.

The following procedures are suggested in this practice analysis, some reactions being conducted with the evolved gas and others with drop portions of the solution.

Separate tests with the evolved gas:

1. For HCN, try the Prussian blue test on drop-reaction paper.
2. For NO_2, use the potassium iodide-starch paper test.
3. For H_2S, the lead acetate test should be performed.
4. For SO_2, use the nitroprusside test, first adding some $HgCl_2$ to the solution.
5. For CO_2, add a few drops of $HgCl_2$ to remove the cyanide ion and a little H_2O_2 to oxidize the H_2S and SO_2, and then hold a drop of $Ba(OH)_2$ solution in the liberated gas.

Separate tests with the solution:

1. For cyanides, try the picric acid reaction. Note that sulfides interfere to some extent.
2. For nitrites, the sulfanilic acid, α-naphthylamine reaction is suitable.
3. For sulfides, the sodium nitroprusside test is recommended.
4. For thiosulfates, a specific test is with the use of antimony trichloride.
5. For sulfites, no good test is available with use of the solution in the presence of interfering ions.

GROUP II. THE $BaCl_2$—$CaCl_2$ GROUP

ARSENITES, $AsO_3^{≡}$	CHROMATES, $CrO_4^{=}$
ARSENATES, $AsO_4^{≡}$	SULFATES, $SO_4^{=}$
PHOSPHATES, $PO_4^{≡}$	BORATES, $BO_3^{≡}$, BO_2^{-}
SILICATES, $SiO_3^{=}$	OXALATES, $C_2O_4^{=}$
FLUORIDES, F^{-}	TARTRATES, $C_4H_4O_6^{=}$

This group is characterized by the precipitation of the barium and calcium salts of these anions when a solution of a mixture of

barium chloride and calcium chloride is added to neutral solutions of these ions. It is to be noted that barium and calcium carbonates and calcium sulfite are also insoluble in a neutral medium, but since carbonates and sulfites have been included in Group I, and are removed before the group test for this group is made in the systematic scheme, they will not be considered here.

Experiment 25.—Dissolve a crystal or two of the sodium or potassium salts of each of the members of this group in about 1 cc. of water in separate test tubes. Make up a solution of $BaCl_2$ and of $CaCl_2$. Try the effect of these two reagents separately on separate drop portions of each of the test solutions. Tabulate the results. In the case of the arsenite, arsenate, phosphate, silicate, chromate, sulfate and metaborate the barium salts are relatively more insoluble than the corresponding calcium salts. In the case of the fluoride, oxalate and tartrate the calcium salts are the more insoluble. In systematic analysis, when testing for this group as a whole, the group reagent consists of a mixture of $BaCl_2$ and $CaCl_2$.

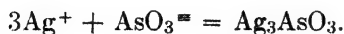
Properties and Tests

ARSENITES, $AsO_3^{\equiv}$; ARSENATES, $AsO_4^{\equiv}$

Arsenic may be present as a constituent of samples of material in the form of a salt of arsenic, as, for example, $AsCl_3$ or $AsCl_5$, i.e., in the cation form; or the element may be present as an arsenite or as an arsenate, i.e., in the anion form. To determine definitely in what form the constituent is present it becomes necessary to test for this element among the anions. Further it sometimes becomes necessary to distinguish between arsenites and arsenates.

The properties which distinguish arsenites from arsenates are shown in the following experiments.

Action of $AgNO_3$.—Place a drop of arsenite solution on a glass slide and add a drop of $AgNO_3$ solution. The yellow precipitate is silver arsenite:

$$3Ag^+ + AsO_3^{\equiv} = \underline{Ag_3AsO_3}.$$

Repeat the experiment using a drop of arsenate solution. A chocolate-brown precipitate of silver arsenate forms:

$$3Ag^+ + AsO_4^{\equiv} = \underline{Ag_3AsO_4}.$$

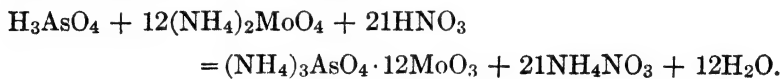
Both precipitates are soluble in dilute HNO_3.

Action of H_2S.—Place a drop of arsenite solution in a centrifuge tube, add a drop of dilute HCl and pass in H_2S. A yellow precipitate of arsenious sulfide, As_2S_3, forms immediately. Repeat, using arsenate test solution. Note that a light yellow precipitate forms very slowly. Heat the tube to facilitate the formation of As_2S_5. Refer to the action of H_2S in connection with the precipitation of the sulfides of arsenic in Group II of the cations.

Tests for Arsenates

Action of $(NH_4)_2MoO_4$.—Add a drop of ammonium molybdate reagent to a drop of arsenite test solution. No precipitate forms.

Add a drop of $(NH_4)_2MoO_4$ to a drop of arsenate test solution acidified with HNO_3. The yellow precipitate is ammonium arsenomolybdate. The reaction is:

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = \underline{(NH_4)_3AsO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O.$$

Phosphates give, with ammonium molybdate, a similar yellow precipitate. This reaction is therefore not specific for arsenates.

A modification of this procedure, suggested by Gutzeit,[1] consists in precipitating the yellow ammonium arsenomolybdate, with a sulfuric acid solution of the reagent, on drop-reaction paper, treating this with a 20 per cent solution of stannous chloride, whereupon a blue stain is obtained. This stain is insoluble in ether, thus distinguishing it from a similar stain, obtained with phosphates, which, according to this investigator, is soluble in ether.

Refer to the discussion of arsenic on page 134 for additional tests for arsenates.[2]

[1] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

[2] See also L. Marrison, Chemistry and Industry **1935**, 872; C. A. 7866 (1935).

PHOSPHATES, $PO_4^{\equiv}$

Phosphorus forms a number of acids, the most important being orthophosphoric acid, H_3PO_4, phosphorous acid and pyrophosphoric acid. The reactions studied here are with the orthophosphate, $PO_4^{\equiv}$, ion. In its properties the $PO_4^{\equiv}$ ion is similar to the $AsO_4^{\equiv}$ ion.

With $AgNO_3$ a yellow precipitate of silver phosphate, Ag_3PO_4, is formed. No precipitate forms with H_2S, in which respect phosphates differ from arsenates, this property enabling one to separate these two ions.

Tests for Phosphates

Action of $(NH_4)_2MoO_4$ and Added Reagents.—To a drop of phosphate test solution, acidified with HNO_3, add a drop of $(NH_4)_2MoO_4$ solution. The yellow precipitate is ammonium phosphomolybdate and is indistinguishable in appearance from the corresponding ammonium arsenomolybdate. The precipitate, however, is soluble in ammonium acetate solution, in which respect it differs from that obtained with arsenates.[1]

In the same way as described under arsenates, the ammonium phosphomolybdate may be reduced with a 20 per cent solution of $SnCl_2$, and the stain, according to Gutzeit,[2] is soluble in ether.

Feigl[3] recommends the following modification of the $(NH_4)_2MoO_4$ test. A drop of test solution and a drop of a tartaric acid solution of the reagent are placed on drop-reaction paper and the spot dried over a heated gauze. Then a drop of an acetic acid solution of benzidine is added and, upon developing with NH_3 fumes, a blue color appears.

Another test suggested by Gutzeit[4] consists in placing a drop of $K_4Fe(CN)_6$ on paper, drying it, adding a drop of phosphate solution and then encircling the spot with a 5 per cent solution of uranyl acetate. A ring, varying from green to brown in color, is the result.

Action of Magnesia Mixture.—Treat a drop of test solution with a drop of magnesia mixture on a glass slide. The white precipitate is $MgNH_4PO_4$. Compare this with the precipitate obtained with a drop of arsenate test solution.

[1] A. I. Sheinkman and N. A. Galetzkii, Farm. Zhur. **1932,** No. 3–4, 120; C. A. 4554 (1932).

[2] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

[3] F. Feigl, Z. anal. Chem. **77**, 299 (1929); C. A. 3873 (1929); Z. anal. Chem. **61**, 454 (1922); C. A. 251 (1923).

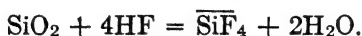
[4] G. Gutzeit, *loc. cit.*

SILICATES, $SiO_3^{=}$

The simplest of the silicic acids known is meta silicic acid, H_2SiO_3, from which the simple silicates such as Na_2SiO_3 are de-

rived. With the exception of the alkali salts of meta silicic acid, all silicates are insoluble in water and most of them insoluble in acids. Fusion of silicates with Na_2CO_3 produces gelatinous silicic acid when the fused mass is dissolved in water and acidified. Sodium silicate solution is used as the test substance in the following experiments.

Silicates are decomposed with hydrofluoric acid, HF, evolving gaseous silicon tetrafluoride, according to the reaction:

$$SiO_2 + 4HF = \overline{SiF_4} + 2H_2O.$$

This is an important analytical property and is utilized in the tests for fluorides.

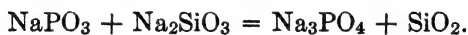
Tests for Silicates

Silicic Acid Test.—Place a drop of a silicate test solution in a centrifuge tube, make the solution basic with NH_4OH and then add two or three drops of NH_4NO_3. The gelatinous white precipitate, semi-colloidal in nature, is H_2SiO_3.

Bead Test for Silicates.—Evaporate a portion of the test solution of Na_2SiO_3 nearly to dryness. In the loop of a platinum wire fuse some " microcosmic salt," $NaNH_4HPO_4$. Sodium metaphosphate, $NaPO_3$, will remain as a bead:

$$NaNH_4HPO_4 = NaPO_3 + \overline{H_2O} + \overline{NH_3}.$$

Dip this bead into the concentrated solution of Na_2SiO_3, and heat in the flame. This will leave SiO_2 in the form of opaque stringers or globules in the otherwise clear bead:

$$NaPO_3 + Na_2SiO_3 = Na_3PO_4 + \underline{SiO_2}.$$

Reaction with $(NH_4)_2MoO_4$ and Benzidine.[1]—Place a drop of test solution and a drop of $(NH_4)_2MoO_4$ on drop-reaction paper. Dry the spot over a heated gauze. Then add a drop of benzidine and a drop of dilute NH_4OH. A blue color develops. It should be noted that arsenates and phosphates interfere; their removal is given under the exercise outlined below, and in the systematic scheme of analysis.

Gutzeit[2] recommends a test quite similar to the above, using $SnCl_2$ to reduce the molybdenum silicate complex. The final color is blue.

[1] F. Feigl and P. Krumholz, Ber. **62B**, 1138 (1929); C. A. 4160 (1929).
[2] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

FLUORIDES, F^-

Most of the fluorides are insoluble in water, the notable exceptions being those of silver, mercury, tin, sodium, potassium and ammonium. Fluorides are decomposed by concentrated H_2SO_4, yielding the free acid, HF, which is a liquid boiling at 19.4° C. The acid attacks glass and other silicates, forming the volatile silicon tetrafluoride according to the reaction, in the case of silica:

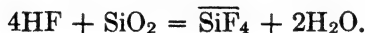
$$SiO_2 + 4HF = \overline{SiF_4} + 2H_2O.$$

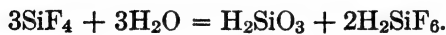
Tests for Fluorides

Etching Test.—Place a few drops of test solution or some powdered CaF_2 in a lead crucible. Coat part of the lower side of a watch glass with hot paraffin or beeswax; when it is cool, with the point of a knife, cut some characters through the wax coating. Then add a few drops of concentrated H_2SO_4 to the crucible, and place the watch glass on the crucible. Cool the watch glass by placing in it some water. Gently warm the crucible. After about ten minutes examine the glass for etching. Silicates and borates interfere with the etching test.[1]

The Water Drop Test.—In a lead crucible place several drops of test solution, some powdered silica and a few drops of concentrated H_2SO_4. Take up a drop of water in the loop of a platinum wire. Gently warm the crucible and hold the drop of water in the vapors. The action taking place can be represented by the reactions:

$$2NaF + H_2SO_4 = 2HF + Na_2SO_4$$

$$4HF + SiO_2 = \overline{SiF_4} + 2H_2O.$$

The SiF_4 reacting with the water forms silicic acid and hydrofluosilicic acid:

$$3SiF_4 + 3H_2O = \underline{H_2SiO_3} + \underline{2H_2SiF_6}.$$

These two products are insoluble in water and render the drop turbid. This test has been modified[2] in that these products are taken up in ammonium molybdate, and treated with benzidine and sodium acetate, a blue reduction product forming.

The zirconium alizarin lake method, first suggested by de Boer[3] and applied by Pavelka,[4] is carried out as follows. Test

papers are prepared by moistening strips of filter paper with a solution of basic zirconium nitrate to which an excess of an alcoholic solution of alizarin has been added. The papers are dried and then moistened first with a 50 per cent solution of acetic acid and then with a drop of the test solution. The red color of the lake is almost completely discharged. Phosphates, oxalates and sulfates interfere with this test.

Pertusi[5] has recently suggested a test for fluorides consisting of using a mixture, in equal parts, of benzidine acetate solution and mercuric succinimide.

[1] Curtman and Auerbach, Chem. News **143**, 180–2 (1931); C. A. 5871 (1931). Curtman, Qualitative Chemical Analysis, p. 378.

[2] F. Feigl and P. Krumholz, Ber. **62B**, 1138 (1929); C. A. 4160 (1929).

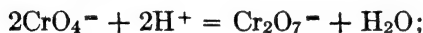
[3] J. de Boer, Chem. Weekblad **21**, 404 (1924); C. A. 793(1925). R. Charonnat, Compt. rend. **199**, 1620 (1934); C. A. 1359 (1935).

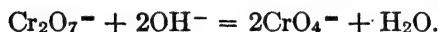
[4] F. Pavelka, Mikrochemie **6**, 149 (1928); C. A. 3871 (1929).

[5] C. Pertusi, Atti III congresso naz. chim. pura applicata **1930**, 573; C. A. 2076 (1931).

CHROMATES, $CrO_4^{=}$; DICHROMATES, $Cr_2O_7^{=}$

Chromates and dichromates are compounds of chromium in which the element is in the acid radical, and the soluble salts ionize to yield the chromate anion, $CrO_4^{=}$, and the dichromate anion, $Cr_2O_7^{=}$. Chromates are transformed into dichromates by increasing the acidity of the solution:

$$2CrO_4^{=} + 2H^+ = Cr_2O_7^{=} + H_2O;$$

and, conversely, the dichromate becomes the chromate ion when the solution is made basic:

$$Cr_2O_7^{=} + 2OH^- = 2CrO_4^{=} + H_2O.$$

Chromate solutions are yellow; dichromate solutions are orange-red in color.

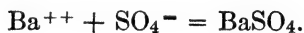
No matter in what form the chromium may be in an original mixture, in a systematic analysis for cations, chromium will be identified in the cation scheme. To ascertain whether the chromium is present in the mixture as a chromic salt, $CrCl_3$ for example, or as a chromate or dichromate it becomes necessary to test for chromates among the anions. In the cation scheme, the identifying tests for chromium are made in a solution in which the

chromium exists as chromate ion. Consequently the tests studied under chromium in the cation scheme apply here.

SULFATES, $SO_4^{=}$

Most of the salts of H_2SO_4 are soluble in water; Ag_2SO_4, $CaSO_4$, $HgSO_4$ and $PbSO_4$ are somewhat soluble, and $SrSO_4$ and $BaSO_4$ are insoluble. $BaSO_4$ is insoluble even in HCl; this is the most characteristic property of this salt.

Barium Chloride Test.—Acidify a drop of sulfate test solution with dilute HCl and then add a drop of $BaCl_2$ reagent. The white precipitate is $BaSO_4$:

$$Ba^{++} + SO_4^{=} = \underline{BaSO_4}.$$

This is the only barium salt of this group of anions which is insoluble in HCl.

The formation of basic mercuric sulfate is made the basis of the sulfate identification by Denigès.[1] This procedure as described by Feigl[2] consists in placing a small amount of the solid salt in a watch glass, adding a drop of the reagent (made by mixing 10 grams of mercuric acetate or nitrate and 1 cc. of HNO_3 in 100 cc. of water) and gently warming. A yellow coloration on the surface shows the presence of sulfates. Gutzeit[3] modified this test by placing a drop of the reagent on black filter paper and adding a drop of the test solution.

[1] G. Denigès, Bull. soc. chim. **23**, 36 (1918); C. A. 889 (1918).
[2] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 314.
[3] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

BORATES, $BO_3^{\equiv}$, BO_2^-, $B_4O_7^{=}$

The commonest acid of boron is orthoboric acid, H_3BO_3. A convenient test solution can be made from borax (sodium tetraborate), $Na_2B_4O_7$. This solution ionizes to form the tetraborate ion, $B_4O_7^{=}$, which undergoes hydrolysis, forming the orthoborate ion, $BO_3^{\equiv}$, and the metaborate ion, BO_2^-.

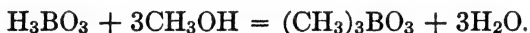
Tests for Borates

Reaction on Turmeric Paper.—Add a drop of dilute HCl to several drops of the borax test solution and moisten a strip of

turmeric test paper with the solution. Dry the test paper. The area turns red. Treat the spot with a dilute solution of NaOH; the spot becomes light blue or green. This reaction is extremely sensitive.

This test is modified, on the micro scale, by using a solution of turmeric instead of test paper, conducting the reaction in a micro crucible or a spot plate, the red color creeping to the edges of the mixture.[1]

Flame Coloration.—Place a drop of test solution in a porcelain crucible; add a drop of concentrated H_2SO_4 and five drops of methyl alcohol. Ignite the vapors. The methylborate burns with a green color.

$$H_3BO_3 + 3CH_3OH = (CH_3)_3BO_3 + 3H_2O.$$

Stahl,[2] who has recently studied the flame colorations with methyl and ethyl alcohol, concludes that the best results are obtained with a reaction mixture of 5 volumes of CH_3OH to 1 volume of concentrated acid.

The volatility and flame color of boron fluoride[3] may also be used as a test for boron, the fluorine being introduced as CaF_2.

Additional tests recently described are: the use of methyl red indicator and mannitol;[4] Congo red;[5] quinalizarin;[6] and carob seed gum.[7] For the application of these reagents the references should be consulted.

[1] W. B. White, Annual Rept. N. Y. Dept. Agr. and Markets **97**, (1930); C. A. 3726 (1930).

[2] W. Stahl, Acta Univ. Latviensis Kim. Fakult. Serija 1, No. 13, 399 (1930); C. A. 1455 (1931). Z. anal. Chem. **101**, 342 (1935); C. A. 5774 (1935).

[3] Curtman, Qualitative Chemical Analysis, p. 368.

[4] A. S. Dodd, Analyst **54**, 282 (1929); C. A. 4645 (1929).

[5] J. Stamm, Pharmacia **1924**; C. A. 2612 (1925).

[6] F. Feigl and P. Krumholz, Mikrochemie, Pregl Festschrift, p. 77 (1929); C. A. 2400 (1930).

[7] R. Hart, Ind. Eng. Chem., Anal. Ed. **2**, 329 (1930); C. A. 4237 (1930).

OXALATES, $C_2O_4^{=}$

The organic acid, oxalic acid, $H_2C_2O_4$ or $\begin{array}{l}COOH\\ |\\ COOH\end{array}$, is a white

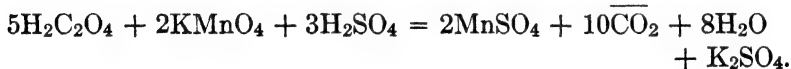
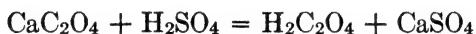
solid crystallizing with two molecules of H_2O. The alkali oxalates are soluble in water. The alkaline earth oxalates and almost all other oxalates are insoluble in water but dissolve in strong acids. Calcium oxalate is insoluble in acetic acid. Oxalates are strong reducing agents, and in an acidified solution reduce such oxidizing agents as $KMnO_4$. On igniting an oxalate, CO_2, CO and H_2O are given off, with little or no charring. If an oxalate is heated with a mixture of concentrated HNO_3 and H_2SO_4, it is destroyed.

Tests for Oxalates

Bleaching Test.—Place a drop of test solution in a centrifuge tube and add a drop or two of $Ca(C_2H_3O_2)_2$ reagent. The precipitate is CaC_2O_4. This is a characteristic reaction of the oxalate ion and is the inverse of the test for calcium.

Centrifuge the mixture, discarding the solution. Dissolve the CaC_2O_4 in dilute H_2SO_4 and add a drop of dilute $KMnO_4$:

$$CaC_2O_4 + H_2SO_4 = H_2C_2O_4 + CaSO_4$$

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + 10\overline{CO_2} + 8H_2O + K_2SO_4.$$

The bleaching of the solution is due to the reducing action of the oxalic acid liberated in dissolving the CaC_2O_4.

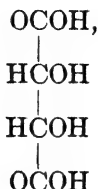
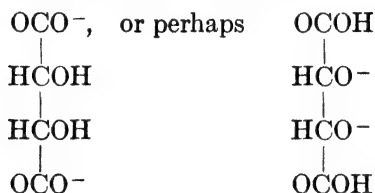
Resorcinol Test.[1]—Place a few drops of test solution in a test tube; add a drop of dilute H_2SO_4 and a speck of magnesium powder. When the metal has dissolved add a dilute solution of resorcinol and carefully run down the sides of the tube five or six drops of concentrated H_2SO_4. A blue ring will form at the junction of the two liquids.

According to Eegriwe,[2] tannic acid may be used to detect oxalic acid, the test being conducted in much the same manner as above, giving a violet-pink coloration with extremely small amounts of oxalate.

[1] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).
[2] E. Eegriwe, Z. anal. Chem. **89**, 121 (1932); C. A. 4769 (1932).

TARTRATES, $C_4H_4O_6^{=}$

Tartaric acid and alkali tartrates are important analytical reagents. The acid is a white crystalline solid having the structural formula

OCOH,
|
HCOH
|
HCOH
|
OCOH

which, on ionizing, yields the tartrate ion,

With many metallic ions, particularly iron, chromium, aluminum, copper and antimony, in basic solutions, soluble complex ions are formed which hinder and interfere with the precipitation of these metals. Citrates, malates, sugars, starches and many other organic materials of this kind behave similarly. It is important therefore to test for and remove substances of this type from samples which are being analyzed for cations.

Tests for Tartrates

Action of Concentrated H_2SO_4.—Place a drop of test solution in a crucible and evaporate the solution to dryness. Then add a drop of concentrated H_2SO_4. Charring of the mass takes place accompanied by the odor of burnt sugar. This is a characteristic property of organic compounds of the type of tartrates. Not only does this furnish a test for tartrates, but by continued action of the H_2SO_4, the substance is completely destroyed by being oxidized, liberating CO_2, CO, H_2O and SO_2 from the H_2SO_4.

Formation of Silver Mirror.—Tartrates will reduce an ammoniacal solution of $AgNO_3$ to metallic silver. In a small test tube place a drop or two of test solution, a few drops of $AgNO_3$ solution

and enough NaOH to form a brown precipitate of Ag_2O. Then dissolve the precipitate with one or two drops of concentrated NH_4OH, adding some NH_4Cl to prevent the possible formation of explosive silver azide, AgN_3. Carefully heat the tube over a micro flame. A deposit of silver in the form of a silver mirror will appear on the walls of the tube.

Resorcinol Test.[1]—This test, recommended by Gutzeit, is conducted as described under oxalates, except that, if one heats the sulfuric acid carefully at the bottom of the tube, a red ring forms in the presence of tartrates.

Eegriwe[2] heats a little of the substance with concentrated H_2SO_4 containing a little tannic acid, a blue, bluish-green or yellowish-green coloration resulting.[3]

[1] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

[2] E. Eegriwe, Z. anal. Chem. **89**, 121 (1932); C. A. 4769 (1932).

[3] See also O. Fürth and H. Herrmann, Biochem. Z. **280**, 448 (1935); C. A. 54 (1936).

EXERCISE. PRACTICE ANALYSIS OF A MIXTURE CONTAINING ARSENITES, ARSENATES, PHOSPHATES, SILICATES AND FLUORIDES. —Make up a water solution of a mixture of the sodium salts of these anions, using enough water to make about 5 cc. of solution. Portions of this mixture are then to be taken for the separations and identifications suggested below.

To about ½ cc. of the solution add, dropwise, $AgNO_3$ reagent. The silver salts will precipitate in the order of their insolubility, and the chocolate brown of the silver arsenate can be observed on top of the yellow Ag_3AsO_3 and Ag_3PO_4 and the white Ag_2SiO_3. Silver fluoride is too soluble to form here.

If a drop of $(NH_4)_2MoO_4$ is added to a drop of the original mixture containing both arsenates and phosphates, the yellow precipitate produced is a mixture of $(NH_4)_3AsO_4 \cdot 12MoO_3$ and $(NH_4)_3PO_4 \cdot 12MoO_3$, and this reaction, without modifications, is therefore not specific. Likewise magnesia mixture cannot be used directly since both $MgNH_4AsO_4$ and $MgNH_4PO_4$ will form.

The use of H_2S will serve in a rough way to distinguish between arsenites and arsenates, the former precipitating rapidly as yellow As_2S_3 and the latter coming down slowly as a yellow mixture of As_2S_5, As_2S_3 and S. Moreover, since the usual tests for arsenates are interfered with by phosphates, H_2S is used to separate the arsenate from the phosphate.

Pass H_2S into about 1 cc. of the sample contained in a centrifuge tube. The immediate formation of a yellow precipitate of As_2S_3 shows the presence of arsenites. The continued formation of yellow precipitates upon further passage of H_2S is due to the slower rate of precipitation of the arsenate. Continue the action until precipitation seems complete. Centrifuge, removing the supernatant liquid to another tube. Test for complete precipitation in the second tube. The supernatant liquid now contains the phosphate, silicate and fluoride ions. To show the presence of $PO_4^{\equiv}$ in this solution, test a drop of it with $(NH_4)_2MoO_4$. The yellow precipitate is $(NH_4)_3PO_4 \cdot 12MoO_3$. Test another drop, made basic with NH_4OH, with magnesia mixture. White $MgNH_4PO_4$ will slowly form. Also perform the following test for phosphates.

Prepare a saturated solution of borax on a spot plate. Dip a strip of filter paper into the supernatant liquid from which arsenates have been removed, then immerse it in the borax solution, add a drop of a 20 per cent solution of $SnCl_2$ and finally a drop of an $(NH_4)_2MoO_4$ solution acidified with dilute H_2SO_4. Dry the test paper and add ether. The blue color should disappear.

In the presence of phosphates and fluorides, the bead test for silicates described on page 196 is suggested.

As a test for fluorides in this mixture, the water drop test, with suitable modifications, should be tried.

EXERCISE. PRACTICE ANALYSIS OF A MIXTURE CONTAINING SULFATES, BORATES, OXALATES AND TARTRATES.—Prepare a mixture of these anions by dissolving the sodium salts in a little water. Use borax to furnish the borate ion. Take separate portions of the mixture for the tests outlined below.

To identify sulfates in this mixture, add a drop of the mixture to a drop of $BaCl_2$ solution and then a drop of concentrated HCl. The white precipitate which remains insoluble in the acid is $BaSO_4$ and constitutes a definite test for the sulfate radical.

The presence of borates may be shown by the following methods: Perform the turmeric paper test by dipping a strip of paper in a drop of the solution acidified with HCl and then drying the paper. A red color first appears, but this is not conclusive evidence for the presence of borates. When the spot is treated with dilute NaOH the red area will become green if borates are present.

Treat a few drops of the test mixture with concentrated H_2SO_4

and methyl alcohol in a crucible. When the vapors are lighted they burn with a green flame.

The test for oxalates depends upon the formation of CaC_2O_4 in a solution acidic with $HC_2H_3O_2$. Take a drop or two of test solution, in a centrifuge tube; add $Ca(C_2H_3O_2)_2$ reagent and a drop of acetic acid. Centrifuge, remove the supernatant solution and to the precipitate add a drop of dilute H_2SO_4 and a tiny drop of $KMnO_4$. The bleaching of the solution shows the presence of the reducing oxalate ion.

Perform the charring test for tartrates by evaporating a portion of the test mixture to dryness and adding a drop of concentrated H_2SO_4. Also perform the mirror test according to the instructions given under Tartrates.

GROUP III. THE $AgNO_3-HNO_3$ GROUP

This group of anions properly embraces the ferrocyanide, $Fe(CN)_6^{----}$; the ferricyanide, $Fe(CN)_6^{\equiv}$; the thiocyanate, CNS^-; the iodide, I^-; the bromide, Br^-; and the chloride, Cl^-, ions. This grouping is based on the fact that a silver nitrate solution, even in the presence of HNO_3, will precipitate the silver salts of these ions. Cyanides also show this behavior, but this ion is not included in this group since its detection has already been considered along with other members of the volatile group. The following experiments form the basis of this grouping.

Experiment 26.—Place a speck of a salt of each of these anions in separate depressions of the spot plate, and dissolve the particles in a drop or two of water. Treat each preparation with a drop of dilute HNO_3, and then add a drop of $AgNO_3$ reagent. The results are here indicated by the following equations:

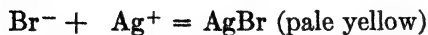
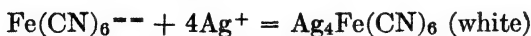
$$Fe(CN)_6^{----} + 4Ag^+ = \underline{Ag_4Fe(CN)_6} \text{ (white)}$$

$$Fe(CN)_6^{\equiv} + 3Ag^+ = \underline{Ag_3Fe(CN)_6} \text{ (reddish-brown)}$$

$$CNS^- + Ag^+ = \underline{AgCNS} \text{ (white)}$$

$$I^- + Ag^+ = \underline{AgI} \text{ (yellow)}$$

$$Br^- + Ag^+ = \underline{AgBr} \text{ (pale yellow)}$$

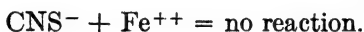
$$Cl^- + Ag^+ = \underline{AgCl} \text{ (white).}$$

In connection with the use of $AgNO_3$ as a test reagent, it is important to know that many other anions are precipitated as water-insoluble silver salts, and that the use of this reagent in a neutral as well as in a nitric acid solution furnishes many helpful clues to the presence of certain anions. Thus in addition to the above-listed silver salts, together with AgCN already referred to, which are insoluble in a nitric acid solution as well as in a neutral medium, the following salts are precipitated by $AgNO_3$ in a neutral solution: Ag_2S (black); Ag_2SO_3 (white); $Ag_2S_2O_3$ (white); Ag_2CO_3 (white); Ag_3AsO_3 (yellow); Ag_3AsO_4 (brown); Ag_3PO_4 (yellow); Ag_2SiO_3 (white); Ag_2SO_4 (white); $AgBO_2$ (white); $Ag_2C_2O_4$ (white, turning brown); $Ag_2C_4H_4O_6$ (white), and Ag_2CrO_4 (red). The nitrite $AgNO_2$ is sparingly soluble, and the fluoride, acetate and nitrate rather highly soluble.

Solutions of iron salts constitute valuable reagents for detecting ferrocyanides, ferricyanides and thiocyanates. This will be evident after performing the following experiment:

Experiment 27.—In three depressions of the spot plate place drops of the ferrocyanide, ferricyanide and thiocyanate solutions, and to each add a drop of freshly prepared $FeSO_4$ or $Fe(NH_4)_2(SO_4)_2$ solution.

$$Fe(CN)_6^{----} + Fe^{++} + 2K^+ = \underline{K_2FeFe(CN)_6} \text{ (white, turning blue)}$$

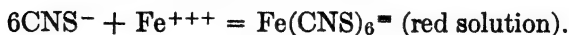
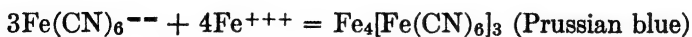
$$2Fe(CN)_6^{\equiv} + 3Fe^{++} = \underline{Fe_3[Fe(CN)_6]_2} \text{ (Turnbull's blue)}$$

$$CNS^- + Fe^{++} = \text{no reaction.}$$

The distinctive feature in these reactions is the formation of Turnbull's blue, a distinctive test for ferricyanides.

Repeat the above experiment, using drops of $FeCl_3$ as test reagent instead of $FeSO_4$.

$$3Fe(CN)_6^{----} + 4Fe^{+++} = \underline{Fe_4[Fe(CN)_6]_3} \text{ (Prussian blue)}$$

$$Fe(CN)_6^{\equiv} + Fe^{+++} = FeFe(CN)_6 \text{ (brown solution)}$$

$$6CNS^- + Fe^{+++} = Fe(CNS)_6^{\equiv} \text{ (red solution).}$$

Here ferric chloride forms Prussian blue with the ferrocyanide ion and an intensely red solution with the thiocyanate ions, both being excellent tests for these two anions.

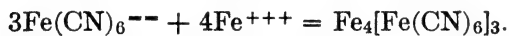
Properties and Tests

FERROCYANIDES, $Fe(CN)_6^{----}$

All ferrocyanides are insoluble in water except those of the alkali and alkaline earth metals. Some of these metals also form insoluble mixed salts of the type $SrK_2Fe(CN)_6$. Soluble ferrocyanides are yellow in color; a number of the insoluble ones are white, but others are colored. These compounds are easily oxidized in solution to ferricyanides by H_2O_2, $KMnO_4$ and other oxidizing agents. They are decomposed by ignition and by heating with strong acids, forming a variety of products such as CO, CO_2, HCN, NH_3, etc., depending upon the conditions under which decomposition takes place.

Tests for Ferrocyanides

Prussian Blue Test.—As was indicated in Experiment 27 (page 206), ferric salts give a good test for this ion and most tests depend ultimately upon this reaction:

$$3Fe(CN)_6^{----} + 4Fe^{+++} = \underline{Fe_4[Fe(CN)_6]_3}.$$

Methods for detecting ferrocyanides in the presence of ferricyanides and thiocyanates have been devised,[1] and one is described in the scheme of analysis for this group (see page 243).

The formation of other colored insoluble ferrocyanides may be useful in confirming the presence of this ion. For example, precipitate copper ferrocyanide, $Cu_2Fe(CN)_6$, by adding a drop of copper test solution to a drop of a ferrocyanide solution on a spot plate and note the brick red color of the precipitate (see page 123). Cobalt salts, used in the same way, give a green precipitate of $Co_2Fe(CN)_6$.

[1] A. Shapovalenko, Ukrain. Khem. Zhur. **4**, Sci. Pt. 303 (1929); C. A. 3458 (1930). T. Pavolini, Ann. chim. applicata **19**, 561 (1929); C. A. 2691 (1930). G. Gutzeit, Helv. Chim. Acta **12**, 829 (1929); C. A. 38 (1930). A. V. Pavlinova and T. N. Bakh, Ukrain. Khem. Zhur. **5**, Sci. Pt. 233 (1930); C. A. 2076 (1931).

FERRICYANIDES, $Fe(CN)_6^{---}$

Ferricyanides are, in general, more soluble than the corresponding ferrocyanides. In particular, the alkali and alkaline earth metals form no insoluble combinations as with ferrocyanides.

In solution, all ferricyanides are characterized by red or reddish-brown colors, but the insoluble compounds show a variety of colors. Ferricyanides may be reduced to ferrocyanides and, like them, are decomposed by strong acids and by ignition, with the formation of similar products.

Tests for Ferricyanides

Ferrous salts are of great importance in the detection of ferricyanides (see Experiment 27). However, other colored precipitates may also be formed as supplementary tests for the presence of this ion. Mix a drop of cadmium test solution with one of a ferricyanide solution on a spot plate and note the orange color of the precipitated cadmium ferricyanide, $Cd_3[Fe(CN)_6]_2$. A cobalt solution, used instead of cadmium, gives a red precipitate, and zinc gives a yellow precipitate.

For the detection of ferricyanides in the presence of ferrocyanides and thiocyanates see the scheme of analysis for this group (see page 243).

THIOCYANATES, CNS^-

Thiocyanates are salts of thiocyanic acid, HCNS, which is an unstable gas at ordinary temperatures. In aqueous solution HCNS is a strong acid. The salts are colorless, excepting, of course, those containing a colored cation.

Thiocyanates resemble the halides in solubility, AgCNS, $Pb(CNS)_2$ and $Cu_2(CNS)_2$ being relatively insoluble and $Hg(CNS)_2$ being only slightly soluble. These insoluble precipitates, however, readily dissolve in excess of alkali thiocyanate forming complex ions of the type $Ag(CNS)_3^{--}$, $Hg(CNS)_4^{--}$.

Tests for Thiocyanates

The reaction with ferric ions (see Experiment 27) is a very important test for thiocyanates. The blue color formed with cobalt salts (page 159) is also a distinctive test. Revise this latter test so that it will serve as a test for a thiocyanate rather than for cobalt, and apply it to a known thiocyanate solution.[1]

[1] For additional tests see: A. J. Folcini, Rev. centro estud. farm. bioquím. **17**, 413 (1928); C. A. 2693 (1930). F. Feigl, Mikrochemie **7**, 10 (1929); C. A. 4421 (1929). A. V. Pavlinova and T. N. Bakh, Ukrain. Khem. Zhur. **5**, Sci. Pt. 233 (German abstract, 234); C. A. 2076 (1931).

IODIDES, I^-

Of the common cations only silver, lead, mercury (-ous) and copper (-ous) form iodides that are insoluble in water. In each case the iodide is more insoluble than the corresponding bromide or chloride. Silver iodide, AgI, a bright yellow compound, is only slightly soluble in NH_4OH, in which respect it differs markedly from AgCl and, to a lesser extent, from AgBr. This property makes it possible to effect a rough separation of AgI from the other two silver salts.

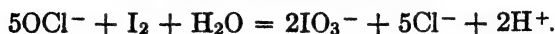
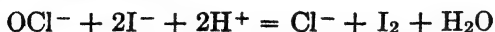
Iodides are very readily oxidized to free I_2, or even to the iodate, IO_3^-. The appearance of purple fumes of I_2 or the violet color of a solution of I_2 in $CHCl_3$, CCl_4 or CS_2 is unmistakable evidence of the presence of this element. Starch is also very commonly used for its detection, the blue starch-iodine color being familiar to all chemistry students. Many different oxidizing agents may be employed to liberate I_2 from an iodide, those more commonly used being chlorine water, sodium hypochlorite,[1] concentrated H_2SO_4, concentrated HNO_3, chloramine T,[2] MnO_2 and H_2SO_4, and $K_2Cr_2O_7$ and H_2SO_4.

Tests for Iodides

Oxidation Test.—To a small amount of a solid iodide, or to a mixture of solid salts containing an iodide, add concentrated H_2SO_4 and warm slowly in a test tube. Purple vapors of iodine appear and may condense along the sides of the tube. Hold a strip of moistened starch (not starch–KI) paper over the mouth of the tube and note the blue color. Cool the tube and add a few drops of $CHCl_3$, CCl_4 or CS_2; shake, and note the color of the lower layer.

To a few drops of a solution of an iodide add several drops of chloroform and then add, drop by drop, a solution of NaOCl, shaking and noting the color of the chloroform layer after the addition of each drop. A violet color soon appears. Continue adding NaOCl. The violet color disappears, owing to oxidation of the iodine to an iodate:

$$OCl^- + 2I^- + 2H^+ = Cl^- + I_2 + H_2O$$

$$5OCl^- + I_2 + H_2O = 2IO_3^- + 5Cl^- + 2H^+.$$

Note that no H_2SO_4 need be added in this case (difference from bromides).

Other Tests

Still other tests are given in the following references.[3] A neat test for iodides is with thallium nitrate. If a drop of an iodide solution, on drop-reaction paper, is held over an open bottle of concentrated HCl and then a drop of a dilute solution of thallium nitrate, $TlNO_3$, added, a yellow precipitate of TlI forms on the paper.[4] Bromides give no similar reaction.

A 1 per cent aqueous solution of palladous chloride,[5] $PdCl_2$, added to a drop of an iodide solution on drop-reaction paper, produces a brownish-black precipitate of PdI_2, insoluble in mineral acids.

[1] F. Harms, Z. physik. chem. Unterricht **42**, 266 (1929); C. A. 661 (1931).

[2] E. M. Gerstenzang, J. Chem. Education **8**, 1187 (1931); ibid. **9**, 318 (1932); C. A. 3272 (1931), 1877 (1932). J. Gorton, Svensk Farm. Tids. **33**, 281 (1929); C. A. 1704 (1930). S. Sussman, J. Chem. Education **9**, 1652 (1932); C. A. 5273 (1932).

[3] For additional tests see: F. Feigl and E. Fränkel, Z. anal. Chem. **91**, 12 (1932); C. A. 683 (1933). C. I. Kruisheer, Z. anal. Chem. **89**, 196 (1932); C. A. 5031 (1932); J. Mikó, Arch. Pharm. **265**, 445 (1927); C. A. 2858 (1927). P. N. van Eck, Pharm. Weekblad **62**, 365 (1925); C. A. 1828 (1925).

[4] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

[5] G. Gutzeit, *loc. cit.*

BROMIDES, Br^-

Group I cations form insoluble bromides as well as chlorides, as might be expected from the close chemical relationship of bromine and chlorine, but the bromides are less soluble than the corresponding chlorides. Bromides are readily oxidized to free bromine, which imparts to chloroform or carbon disulfide a brown or reddish-brown color. These two properties are the basis of several tests for the element. The color and odor of free bromine are characteristic and may serve as evidence of its presence when it has been set free by an oxidizing agent. For this oxidation sodium hypochlorite and H_2SO_4,[1] chromic acid ($K_2Cr_2O_7$ and H_2SO_4), chlorine water, MnO_2 and H_2SO_4, chloramine or chloramine T[2] may be used.[3]

Tests for Bromides

Oxidation Test.—To a few drops of a bromide solution in a test tube add several drops of chloroform (or carbon disulfide) and a small amount of one of the oxidizing agents mentioned

above (NaOCl is especially recommended). Shake the mixture and then note the color in the chloroform layer.

Fluorescein Test.[4]—This reagent, which forms a yellow solution in 50 per cent alcohol, reacts with free bromine to give tetrabromo-fluorescein or eosin (red ink). Saturate a strip of filter paper with the reagent solution (or moisten a strip of prepared fluorescein paper), and hold it over the mouth of a test tube containing a mixture of a bromide, $K_2Cr_2O_7$ and H_2SO_4. Warm gently. The paper assumes a red color. Iodides interfere with this test.

Fuchsin-Bisulfite Test.[5]—If sodium bisulfite, $NaHSO_3$, is added to a solution of fuchsin, the solution, originally red, is decolorized. Upon the addition of free bromine to such a solution a blue or violet dye is formed. Carry out this test in exactly the same way as the preceding one, being careful not to boil the solution.[6]

[1] F. Harms, Z. physik. chem. Unterricht **42**, 266 (1929); C. A. 661 (1931).

[2] M. Markees, Pharm. Acta Helv. **6**, 106 (1931); C. A. 3332 (1932). E. M. Gerstenzang, J. Chem. Education **8**, 1187 (1931); **9**, 318 (1932); C. A. 3272 (1931); 1877 (1932).

[3] Cf. J. Mikó, Arch. Pharm. **265**, 445 (1927); C. A. 2858 (1927).

[4] R. Lorenz, E. Grau and E. Bergheimer, Z. anorg. allgem. Chem. **136**, 90 (1924); C. A. 3020 (1924). H. Baines, J. Soc. Chem. Ind. **47**, 11 (1928); C. A. 1116 (1928). A. V. Pavlinova, Ukrain. Khem. Zhur. **5**, Sci. pt. 231 (1930); C. A. 2076 (1931). E. Murmann, Oesterr. Chem.-Ztg. **32**, 36 (1929); C. A. 3188 (1929).

[5] G. Scheuing and O. Schaaff, Ber. **56B**, 1588 (1923); C. A. 250 (1924). I. Guareschi, Atti accad. sci. Torino **48**, 4 (1913); C. A. 3286 (1913), and other papers.

[6] For additional tests see: G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929). P. N. van Eck, Pharm. Weekblad **62**, 365 (1925); C. A. 1828 (1925).

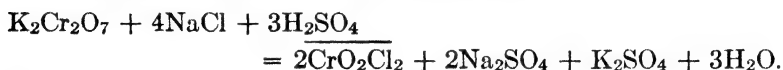
CHLORIDES, Cl^-

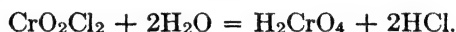
With the exception of AgCl and Hg_2Cl_2 all normal chlorides are soluble in water, although the solubility of $PbCl_2$ and Cu_2Cl_2 is quite low. Contrary to what would be expected from the solubility product principle, high concentrations of HCl or of chloride ions increase the solubility of a number of chlorides, including AgCl, Hg_2Cl_2 and $PbCl_2$. The explanation is that probably complex ions of the type $AgCl_2^-$ are formed. The properties and behavior of the insoluble chlorides have already been considered in connection with the discussion of the cations. The solubility of

AgCl in NH_4OH and its reprecipitability with HNO_3 may be utilized as a test for Cl^- in the absence of CN^-, Br^- and I^-.

Tests for Chlorides

Chromyl Chloride Test.—Heat a small quantity of a solid chloride with a little solid $K_2Cr_2O_7$ and a few drops of concentrated H_2SO_4 in a test tube. Hold over the mouth of the tube a drop of a 3 per cent solution of H_2O_2 held in a loop of platinum wire or spread on a piece of porcelain. The H_2O_2 turns an intense blue, owing to the formation of perchromic acid.[1] Chromyl chloride, CrO_2Cl_2, is formed in the test tube:

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O.$$

The chromyl chloride dissolves in the water of the H_2O_2 solution with the formation of chromic acid, which then reacts with H_2O_2 as previously discussed (see page 151):

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Nitrates interfere with the test as given by forming nitrosyl chloride, NOCl. Diphenyl-carbazide solution may be used instead of H_2O_2, in which case the color obtained is a violet-red.[2]

Although many tests using organic reagents are available for the detection of free chlorine, there are few, if any, for the detection of the chloride ion. However, chlorides may be quite readily oxidized by treatment with $KMnO_4$ in the presence of H_2SO_4, after which the tests may be applied. Inasmuch as these reactions depend upon the oxidizing power of Cl_2, other oxidizing agents will often interfere.

Probably the best known of the tests for free chlorine is that with starch–KI paper.

Most of the other tests involve organic amines, which are oxidized by Cl_2 with the formation of colored (usually blue or red) compounds. Among those that have been mentioned are aniline, *o*-toluidine, diphenyl-amine sulfate,[3] *o*-tolidine and dimethyl-*p*-phenylene diamine hydrochloride.[4,5]

[1] G. G. Longinescu and I. I. Prundeanu, Bul. chim. soc. romÂne chim. **34**, Nos. 1–6 (1931); C. A. 45 (1933).

[2] Feigl, Tüpfelreaktionen, 2nd ed., p. 276.

[3] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929).

[4] K. Alfthan and A. C. Jarvis, J. Am. Water Works Assoc. **20**, 407 (1928); C. A. 4681 (1928).

[5] For additional tests see: G. Gutzeit, *loc. cit.* A. Novelli, Rev. farm. (Buenos Aires) [2] **2**, 205 (1929); C. A. 4422 (1929). J. Stiepovich and A. Sà, Rev. cent. estud. farm. bioquím. **16**, 384 (1927); C. A. 1580 (1929). E. Eegriwe, Z. anal. Chem. **74**, 225 (1928); C. A. 3859 (1928). G. T. Mikhalchishin, Ukrain. Khem. Zhur. **6**, Tech. Wiss. Teil 183 (1932); C. A. 3204 (1932).

GROUP IV. THE SOLUBLE ANION GROUP

NITRATES, NO_3^-

All metal nitrates are soluble in water, but some form insoluble basic salts by hydrolysis, e.g., $BiONO_3$. Nitrates are strong oxidizing agents and, like nitrites, form a series of successive reduction products, the end product formed in any case depending upon the reducing agent and the conditions of temperature, concentration and other factors. Thus, NO_2, NO, N_2O, N_2, NH_2OH (hydroxylamine) and NH_3 may be formed. As was previously mentioned (see under Nitrites), nitrates are decomposed by heating with the formation of some nitrite, and nitrites are decomposed by acids with the formation of some nitrate; also, oxidizing and reducing agents may change one to the other, so the two will often be found together and it is difficult to determine whether both are present independently or whether one has been derived from the other.

Tests for Nitrates

In the absence of nitrites, nitrates may be detected by reduction to nitrite and applying the tests already described. For the reduction, sodium amalgam, lead formate, aluminum and NaOH or other reducing agents may be used. Reduction with lead formate followed by the test with sulfanilic acid and α-naphthylamine, as described under nitrites, has been especially recommended.[1a]

The ferrous sulfate test[1] may also be tried in the same way as for nitrites (q.v.) and, if H_2SO_4 is used, can be employed only in the absence of nitrites.

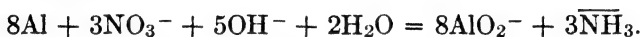
The diphenyl-amine test[2] also is carried out on the solution as described under nitrites. It should be kept in mind that other oxidizing substances interfere. Diphenyl-benzidine, used in the same way, is said to be more sensitive.[3]

Brucine Test.[4]—Dissolve a few crystals of brucine (an alkaloid obtained from nux vomica) in concentrated H_2SO_4 on the spot plate and add to the solution a drop of nitrate test solution. A

deep red color appears but a change to a yellowish tint soon takes place. The addition of $SnCl_2$ then gives a violet color. Nitrites, unless they contain some nitrate, do not give this test, but chlorates interfere.

Ammonia Test.—To a few drops of test solution in a test tube add dilute NaOH and then some aluminum powder or a bit of foil. Ammonia is evolved and may be detected by using the tests described under ammonium. NH_4^+ must, of course, be absent.

The reaction is:

$$8Al + 3NO_3^- + 5OH^- + 2H_2O = 8AlO_2^- + 3\overline{NH_3}.$$

Nitron Test.[5]—This reagent, 1, 4-diphenyl-3, 5-endanilo-dihydro-triazol, $C_6H_5—N—CH=(NC_6H_5)_2=C=N$ (the two N atoms joined by a bond), forms an insoluble compound with a nitrate. The usual solvent for the reagent is acetic acid, but this solution is not stable and must be renewed at frequent intervals. If formic acid is used as the solvent, the reagent, for which the name "fornitrol" has been suggested, is considerably more stable.[6] To perform the test, place a drop of nitrate test solution on a glass slide and add a drop of the reagent solution. A white precipitate is obtained. The precipitate is sufficiently insoluble to serve for the gravimetric determination of nitrates.

Additional Tests

Pyrogallol[7] dissolved in a nitrate solution and treated with concentrated H_2SO_4 gives a brown or yellow coloration.

If benzene is added to a nitrate solution acidified with H_2SO_4, nitrobenzene is formed, and this, upon reduction with zinc, produces aniline. Evaporation with $HgCl_2$ then forms fuchsin which imparts a reddish-violet color to alcohol.[8]

A test that may be used in the presence of nitrite is carried out by adding a solid nitrate and a little $NaNO_2$ to a cold solution of *o*-cresol. A solution is obtained which appears deep green by reflected light and crimson or purple by transmitted light.[9, 10]

REFERENCES TO NITRATES

[1a] F. Hahn and G. Jaeger, Ber. **58B**, 2335 (1925); C. A. 158 (1926).

[1] For modifications and discussions of this test see: E. Schröer, Z. anorg. allgem. Chem. **202**, 382 (1931); C. A. 939 (1932). C. Faurholt, Ber. **56B**,

337 (1922); C. A. 1199 (1923). P. Popov, Ukrain. Khem. Zhur. **2**, 391 (1926); C. A. 1746 (1928).

[2] G. Karoglanov, Z. anal. Chem. **62**, 217 (1923); C. A. 1771 (1923). R. Krauer, Chim. ind. (Brazil) **1**, 143 (1926); C. A. 1777 (1927). Chimica (Brazil) **1**, 122 (1933); C. A. 5270 (1933). A. Weinhagen, J. Am. Chem. Soc. **43**, 685 (1921); C. A. 1719 (1921).

[3] H. Riehm, Z. anal. Chem. **81**, 439 (1930); C. A. 55 (1931).

[4] G. Gutzeit, Helv. Chim. Acta **12**, 713 (1929); C. A. 4645 (1929). I. Korenman, Z. anal. Chem. **93**, 438 (1933); C. A. 5022 (1933).

[5] M. Busch, Ber. **38**, 861 (1905); **39**, 1401 (1906).

[6] Anon., Ann. chim. anal. chim. appl. **3**, 207 (1921); C. A. 3431 (1921). Gutzeit, Ref. 4.

[7] Cf. L. de Nardo, Compt. rend. **188**, 563 (1929); C. A. 2123 (1929).

[8] G. Longinescu and T. Pirtea, Bul. chim. soc. române chim. **34**, Nos. 1–6, 3 pp. (1931); C. A. 45 (1933). G. Longinescu and G. Chaborski, Bull. acad. Roumaine **6**, 176 (1922). Ind. chim. **9**, 67 (1922); C. A. 1546 (1922).

[9] A. Ware, Analyst **52**, 332 (1927); C. A. 2629 (1927).

[10] For other tests see: G. Gutzeit, Ref. 4. L. Desvergnes, Ann. chim. anal. chim. appl. **6**, 102 (1924); C. A. 1799 (1924). H. Wolf and E. Heymann, Z. angew. Chem. **37**, 195 (1924); C. A. 2661 (1924). L. Ekkert, Pharm. Zentralhalle **66**, 733 (1925); C. A. 350 (1926). E. Eegriwe, Z. anal. Chem. **69**, 382 (1926); C. A. 873 (1927). C. Marvel and du Vigneaud, J. Am. Chem. Soc. **46**, 2661 (1924); C. A. 449 (1925). S. Vâgi, Z. anal. Chem. **66**, 14 (1925); C. A. 2000 (1925). P. van Eck, Pharm. Weekblad **62**, 365 (1925); C. A. 1828 (1925). I. Nixon, Chem. News **126**, 261 (1923); C. A. 2091 (1923). D. Buznea and R. Cernatesco, Ann. sci. univ. Jassy **14**, 302 (1927); C. A. 1297 (1928).

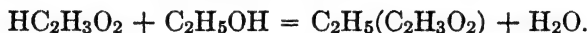
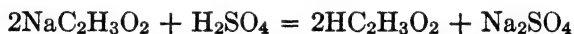
ACETATES, $C_2H_3O_2^-$

Acetic acid, one of the few organic compounds ordinarily considered in inorganic qualitative analytical work, is most familiar as the acid of vinegar. Its normal salts are all soluble in water but, as is true of nitrates, insoluble basic salts, e.g., $Fe(OH)_2C_2H_3O_2$, may be formed. The formation of the red basic ferric acetate upon boiling a mixture of an acetate and $FeCl_3$ (partially neutralized with NH_4OH, if necessary) has been used to detect the acetate ion, but the test is not very reliable.[1] Acetic acid is readily displaced from its salts by stronger acids; hence, by noting the odor when a compound is warmed with H_2SO_4, evidence of the presence of an acetate may often be obtained.

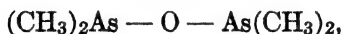
Ester Formation Test.—By the reaction of acetic acid with an alcohol in the presence of a dehydrating agent, e.g., H_2SO_4, an ester is formed, which may be recognized by its distinctive odor. For this reaction methyl or ethyl alcohol is generally used, the ester formed with either having a pleasant, fruity odor. However,

the use of isoamyl alcohol, $C_5H_{11}OH$, has the advantage that the odor of the isoamyl acetate (" banana oil ") formed is more readily distinguished from that of the alcohol itself than is the case with methyl or, especially, with ethyl alcohol. To perform the test, place a few drops of acetate test solution in a crucible, add several drops of one of the above-mentioned alcohols and then a volume of concentrated H_2SO_4 equal to the total volume already present. Warm gently and cautiously smell the contents of the crucible. In making a test on an unknown sample it is well to run a parallel test with a known acetate and compare the odors of the two crucibles. The reactions, using a typical acetate and a typical alcohol, are:

$$2NaC_2H_3O_2 + H_2SO_4 = 2HC_2H_3O_2 + Na_2SO_4$$

$$HC_2H_3O_2 + C_2H_5OH = C_2H_5(C_2H_3O_2) + H_2O.$$

Lanthanum Nitrate Test.[2]—Place a drop or two of acetate test solution in a crucible and add a drop of a 5 per cent solution of lanthanum nitrate, $La(NO_3)_3$. Now add a drop of a dilute ($N/50$) solution of iodine in alcohol and, finally, several drops of dilute NH_4OH. A blue color, very similar to that produced by iodine and starch, may appear in a short time. If not, slowly heat the mixture to boiling and the color will become evident. The mechanism of the color formation is not completely understood; it is probably due to a solid solution of iodine in the precipitated basic lanthanum acetate rather than to a definite compound. Anions that precipitate lanthanum, e.g., $SO_4^{=}$, $PO_4^{\equiv}$, $C_2O_4^{=}$, F^-, interfere, as do cations that are precipitated by NH_4OH.

If a solid acetate is ignited with As_2O_3, cacodyl oxide,

$$(CH_3)_2As — O — As(CH_3)_2,$$

which has a characteristic garlicky odor, is produced. This compound is poisonous and should be smelled cautiously.

[1] L. Curtman and B. Harris, J. Am. Chem. Soc. **39**, 1315 (1917); C. A. 2177 (1917). E. Tschirch, Oesterr. Chem.-Ztg. **34**, 38 (1931); C. A. 2665 (1931). Cf. L. Curtman, D. Broggi and V. Fourman, Chem. News **120**, 230 (1920); C. A. 2594 (1920).

[2] D. Krüger and E. Tschirch, Ber. **62B**, 2776 (1929); C. A. 2401 (1930). Mikrochemie [N.S.] **2**, 337 (1930); C. A. 894 (1931). Pharm. Zentralhalle **71**, 145 (1930); C. A. 2083 (1930). Pharm. Acta Helv. **5**, 25 (1930); C. A. 5002 (1930).

PART IV

SYSTEMATIC MICROANALYSIS

A complete systematic analysis involves the detection of both cations and anions in samples of material of unknown composition. The steps involved in such an analysis are:

A. The Preliminary Examination.
B. Systematic Cation Analysis.
C. Systematic Anion Analysis.
D. The Analysis of the Insoluble Residue.

Several procedures have been devised for systematic microanalysis. Gutzeit[1] has worked out a scheme in which specific tests are made on solutions of the sample obtained by the use of (*a*) sodium hydroxide; (*b*) sodium carbonate; (*c*) nitric acid; (*d*) aqua regia. A cation scheme has been devised by Heller and Krumholz[2] which makes use of the conventional macro group precipitants. Feigl[3] describes a method of Krumholz in which the cations of Groups II, III and IV may be separated after treating a solid mixture with concentrated hydrochloric acid and bromine water. A scheme for alloys using the drop-reaction method has been worked out by Heller.[4] A procedure for the identification of the anions in a mixture has been suggested by Feigl.[5] A scheme of systematic analysis has also been devised by van Nieuwenburg.[6]

[1] G. Gutzeit, Helv. Chim. Acta **12**, 829 (1929); C. A. 38 (1930).
[2] K. Heller and P. Krumholz, Mikrochemie **7**, 213 (1929); C. A. 1818 (1930).
[3] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 347.
[4] K. Heller, Mikrochemie **8**, 33 (1930); C. A. 1597 (1930).
[5] F. Feigl, Tüpfelreaktionen, 2nd ed., p. 351. Z. anal. Chem. 57, 135 (1918); C. A. 2173 (1918).
[6] C. J. van Nieuwenburg, Mikrochemie **3**, 199 (1931); C. A. 2935 (1931). C. J. van Nieuwenburg and G. Dulfer, "A Short Manual of Systematic Qualitative Analysis by Means of Modern Drop Reaction," 2nd ed. Amsterdam: D. B. Centen (1935).

A. THE PRELIMINARY EXAMINATION OF THE SAMPLE

The sample may consist of a solution of cations and anions and may or may not contain a sediment or residue. On the other hand, the sample may be a solid such as a metal, an alloy or a salt, or it may be a mixture of salts or other compounds.

A preliminary physical examination may give some indications of the probable composition of the sample. If the sample is a solution note its color, odor and reaction to litmus paper. Also, if a sediment is present, note the color and whether finely divided, gelatinous or curdy. If the sample is a powder examine it with a hand lens and separate as many components as possible; note the colors and other physical characteristics. After initial examination, a lumpy solid should be powdered and further examined.

A test should be made for the presence of organic material. Add a drop of concentrated sulfuric acid to a portion of the unknown in a crucible. Warm gently. A charring indicates that organic matter is present.

Next the action of water and acids on the unknown should be tested. Add a few drops of water to a very small portion of the solid sample. If the sample is completely water soluble, some idea of the possible compounds present may be had by referring to the solubility chart and noting those compounds which are water soluble.

A colored solution may be due to the presence of water-soluble salts of copper, cobalt, nickel, iron or chromium, or to soluble chromates, dichromates, ferrocyanides or ferricyanides. Test a drop of the solution with litmus paper; an alkaline reaction will indicate a free base or salts which have hydrolyzed to give a basic solution, such as carbonates, sulfides, phosphates and borates; an acid reaction will indicate free acid, an acid salt or salts of heavy metals such as $FeCl_3$ which give an acid hydrolysis.

If the sample does not dissolve completely in water, add a little HCl. If this does not dissolve all the sample, use a new portion of the sample and note the effect of HNO_3.

These simple preliminary tests will determine the best solvent to use in the preparation of a portion of the sample for the cation analysis.

B. SYSTEMATIC CATION ANALYSIS

The first consideration here is the amount of sample to take for the cation analysis. If the sample is a solution, with or without a sediment or precipitate, it is presumed that 1 cc. of the well-shaken sample will contain a sufficient quantity of each constituent to give decisive tests for each cation present. With alloys, as for example, a sample of brass, provision must be made for the detection of the lead, tin and iron which are present in small quantity, frequently less than 1 per cent. Though the standard of sensitivity for microchemical tests is 0.001 mg. (1 gamma, γ, or 1 microgram), for which 1 mg. of the sample of alloy might suffice, a 10-mg. sample is here recommended.

With solid samples consisting of one or more solid salts, the relative proportions of the anions and cations as well as the varying amounts of the different salts present must be taken into consideration. For example, in a 1-mg. sample of KCl, there are approximately 0.52 mg. of potassium and 0.48 mg. of chloride, and these amounts are well above the sensitivity of the tests for the potassium and the chloride ion. But in $HgCl_2$ the proportion of mercury to chloride is much greater and in other cases might be much smaller. On account of the widely varying proportions of cations to anions the arbitrary rule is made that the cation content will be assumed equal to the anion content; in other words one half of the sample is considered to consist of metallic constituents and the other half of acid radicals. In order, then, to provide a solution of the sample for the cation analysis such that the total cation content will be 10 mg., it is necessary to take at least 20 mg. of the sample. This should generally be sufficient for the detection of the several cations which might be present unless one of the components should happen to be present as a mere trace, in which event a much greater amount of sample must be taken in a repeat analysis. In general, the smaller the amount of a constituent present, the greater the weight of sample. The analyst must be guided by the nature, source and history of the sample if traces of certain constituents are suspected and accordingly judge the amount of sample to take.

The next consideration is the preparation of a solution of the sample for the systematic cation analysis and the removal of constituents which would interfere with the detection of the cations.

The preliminary examination will have revealed something regarding the solubility of the sample. A water-soluble sample is comparatively simple in its composition. Nitric acid is the most generally used solvent since there are very few compounds which are not dissolved by it. Certain salts of bismuth, antimony and tin, though not soluble in nitric acid, are soluble in hydrochloric acid. Aqua regia will dissolve a few additional compounds which resist the separate action of HNO_3 and HCl.

Most of the anions interfere in one way or another with the cation analysis. Thus, if halides are contained in the sample along with salts of silver, mercurous mercury or lead, or if HCl is used in dissolving the sample, the insoluble halides of these metals will be precipitated and remain insoluble in the acids used as solvents. Strong oxidizing agents interfere by acting on the H_2S used in the precipitation of Group II. Salts of weak acids, particularly acetates, interfere with the regulation of the acidity of the solution during the precipitation with H_2S. Organic matter hinders the precipitation of certain cations, particularly aluminum and chromium. Phosphates, oxalates and tartrates, and in general, the anions of the $BaCl_2$–$CaCl_2$ group, cause the premature precipitation of the alkaline earth group. The treatment given the sample as recommended below will eliminate most of these troublesome anions with the exception of oxalates and phosphates and possibly tartrates.

Preparation of the Cation Solution

Except for certain artificial student samples, where arbitrary limitations may be placed on the nature or contents and for which it is best that the instructor give special directions, the sample weighing about 20 mg. should be treated in a crucible with 1 cc. of either dilute or concentrated HNO_3, as found necessary in the preliminary examination. The solution is then boiled, a little concentrated HCl added, if found necessary according to the previous trial, and the solution evaporated nearly to dryness. This treatment will volatilize most of the objectionable anions and will remove most of the oxidizing solvent. Enough water is then added to make up the solution to approximately 1 cc. and the solution centrifuged, if a residue remains. The insoluble residue is set aside for later examination (see page 245), and the solution is analyzed for cations.

Analysis of Group I

This group includes silver, mercurous mercury and possibly lead. If HCl was used in getting the sample into solution, the cations of this group will have been precipitated as chlorides and must be tested for according to the procedures described under the analysis of the "Insoluble Residue"; in this case, take 1 cc. of the solution and proceed with the systematic analysis of Group II. Chlorides, bromides and iodides, if present as constituents of the sample, will likewise precipitate the cations of this group.

If HCl has not been used in dissolving the sample, place 1 cc. of the solution in a 3-cc. centrifuge tube. If the solution is basic, neutralize it with concentrated HCl by carefully adding the acid, stirring with a platinum wire and touching the wire to a strip of neutral litmus paper.

After the solution has been neutralized, add one drop of concentrated HCl and stir thoroughly with a platinum wire. A turbidity which clears on addition of HCl indicates the presence of the hydrolyzed salts of antimony, tin or bismuth. If a permanent precipitate forms, showing that members of this group are present, follow the procedure for this group; if not, pass directly to the analysis of Group II. Place a cork provided with a hook in the centrifuge tube; place a similar sized tube in the other container and centrifuge. After centrifuging, remove the tube with the aid of a wire hook. Add another drop of concentrated HCl to test for complete precipitation. After complete precipitation, draw off the clear, supernatant liquid with the capillary pipet and reserve this for analysis of subsequent groups.

Detection of Lead.—Add one or two drops of distilled water to the residue in the centrifuge tube, heat, stir with a platinum wire, centrifuge, remove the supernatant liquid to a test tube and place a drop of it on a glass slide and add a drop of K_2CrO_4 solution. A yellow precipitate of $PbCrO_4$ shows the presence of lead.

To further test for the presence of lead, place a drop of 3 per cent H_2O_2 on drop-reaction paper, add a drop of dilute NH_4OH and then a drop of the supernatant liquid from the centrifuge tube. After allowing the spot mixture to stand for a minute or so, add a drop of tetramethyl-diamino-diphenyl-methane reagent. A blue color shows the presence of lead.

The failure to obtain a positive test for lead by the use of either

K_2CrO_4 or tetramethyl-diamino-diphenyl-methane is not conclusive proof that the sample does not contain lead; it may mean that the sample does not contain enough lead to be precipitated as $PbCl_2$ in this group. If lead is not found here, it should be carefully tested for in Group II.

Detection of Silver.—If lead has been shown to be present, wash the residue with hot water until the washings no longer show a test for this ion. After the complete removal of lead, add one or two drops of concentrated NH_4OH, stir thoroughly, warm and centrifuge. A blackening of the residue on the addition of NH_4OH indicates mercury. After centrifuging, draw off the supernatant liquid with a capillary pipet, transferring one drop to a glass slide. Acidify the liquid on the slide with concentrated HNO_3. The appearance of a white precipitate of AgCl on acidification with HNO_3 shows the presence of silver.

Transfer another drop to a spot plate. Add a drop of KCN, then one of dimethyl-amino-benzylidine-rhodanine reagent, and acidify with HNO_3. A red or red-violet color proves the presence of silver.

Detection of Mercury.—If a black residue remains in the centrifuge tube after treatment with NH_4OH, pipet off the solution, add a crystal of $KClO_3$ and a drop of concentrated HCl, avoiding an excess; *warm carefully.* Transfer the solution to a crucible and continue the gentle heating until chlorine gas is no longer given off; this will be indicated by the disappearance of a yellow color in the solution or by the non-appearance of a blue color on moist starch-potassium iodide paper held in the vapors escaping from the centrifuge tube. After all the chlorine has been removed, add several drops of $SnCl_2$ to a portion of the clear solution. A white or gray precipitate proves the presence of mercury, which was present in the original sample in the mercurous condition.

Place a drop of diphenyl-carbazide solution on the spot plate; add a drop of Na_2CO_3 solution and then a drop of the above solution. A violet to blue color confirms the presence of mercury.

Precipitation and Division of Group II

This group contains the ions of mercuric mercury, lead, bismuth, copper, cadmium, arsenic, antimony and tin.

Group Precipitation.—Place the solution, obtained after removal of Group I, in a large centrifuge tube. Neutralize with concentrated NH_4OH by adding it from a capillary pipet, stirring with a platinum wire and touching the platinum wire to neutral litmus paper. Add a crystal of NH_4I, and make the solution acid to methyl orange paper by carefully adding concentrated HCl from a capillary pipet.

After acidifying, warm the centrifuge tube carefully; then pass in H_2S, tapping the tube frequently meanwhile. After the gas has been passed in for about one minute, remove the tube, insert a cork with a hook and centrifuge the mixture. After centrifuging, pass in more H_2S to test for complete precipitation. Continue the procedure until sulfides no longer form in the clear, supernatant liquid.

After precipitation has been shown to be complete, draw off the supernatant liquid with a capillary pipet and transfer it to a marked test tube or centrifuge tube; this liquid contains Groups III–IV–V; boil it to remove H_2S. Add several drops of water to the residue, stir well with a platinum wire and then heat the tube *gently*. After heating, centrifuge, remove the clear liquid and add it to the solution containing Groups III–IV–V. Repeat the washing until the solution shows only a slight acidity; discard the last washings.

Separation into Subgroups A and B.—Add five to ten drops of Na_2S_2 to the residue in the centrifuge tube, stir the residue with a platinum wire and warm gently for at least one minute. Centrifuge and then remove the supernatant liquid to another marked centrifuge tube; this liquid contains the members of Division B, namely, arsenic, antimony and tin in the form of $AsS_4^{\equiv}$, $SbS_4^{\equiv}$ and $SnS_3^{=}$; mercury may also be present in small quantity as $HgS_2^{=}$. The residue may contain mercury, lead, bismuth, copper and cadmium in the form of their sulfides; it is designated as Division A.

Add three more drops of Na_2S_2 to the residue, add three drops of H_2O; stir, warm, centrifuge and add this solution to that retained above. Repeat this last process until extraction is complete; discard these last washings. To test for the complete extraction of the members of Division B, place a drop of the final washings on a glass slide and a drop of Na_2S_2 on the same slide, acidify each drop with dilute HCl and compare the two. In the

case of the Na_2S_2 a white precipitate of sulfur is formed; colored precipitates of the sulfides of Division B will result in the other drop if the extraction has not been complete.

Analysis of Division A, Group II

Wash the residue, which may contain HgS, PbS, Bi_2S_3, CuS and CdS, with warm water until the washings show only a faint basic reaction. Now add to the residue three drops of dilute HNO_3 and three drops of H_2O. **Boil carefully.** Centrifuge and remove the supernatant liquid to a crucible. Repeat this treatment with two drops more of acid and two drops of water, adding the liquid to that removed above. This treatment dissolves PbS, Bi_2S_3, CuS and CdS, leaving HgS and perhaps some S as a residue.

Detection of Mercury.—If a black residue remains after the HNO_3 treatment, add one or two drops of concentrated HCl and a crystal of $KClO_3$. If the residue dissolves, transfer the solution to another crucible and heat carefully until all the chlorine gas is driven off as shown by the disappearance of a yellow color in the solution or by the non-appearance of a blue color on potassium iodide-starch paper. After the complete removal of chlorine add several drops of $SnCl_2$ to a portion of the solution. A white or gray precipitate indicates the presence of mercury.

Place a drop of diphenyl-carbazide solution on a spot plate; add one drop of Na_2CO_3 solution and then a drop of the solution. A violet or blue color proves the presence of mercury.

Separation and Detection of Lead.—Add three drops of concentrated H_2SO_4 to the solution from the separation of HgS. Boil carefully until dense white fumes of SO_3 appear. Draw up the liquid from the crucible with a pipet and allow it to drop slowly into a centrifuge tube containing two or three drops of water. Centrifuge, and if lead is present a white precipitate of $PbSO_4$ will be found on the bottom of the tube. Remove the liquid to another centrifuge tube. This liquid may contain Bi^{+++}, Cu^{++} and Cd^{++}.

Wash the residue of $PbSO_4$ with two to four drops of water, centrifuge and add the washings to the above solution. Now add two drops of $NH_4C_2H_3O_2$ to the white residue and heat carefully.

After the residue has dissolved add a drop of K_2CrO_4 reagent to a drop of the solution. A yellow precipitate of $PbCrO_4$ shows the presence of lead. The test for lead should be confirmed by applying the tetramethyl-diamino-diphenyl-methane test to another portion of the solution.

Separation and Detection of Bismuth.—Add concentrated NH_4OH to the solution from which lead has been removed and which may contain Bi^{+++}, Cu^{++} and Cd^{++}. A white precipitate forming at this time is probably $Bi(OH)_3$. Continue addition of NH_4OH, with stirring, until the solution is definitely basic. If Cu^{++} is present the solution may become blue at this point. Centrifuge, remove the liquid and place it in a test tube or centrifuge tube. Wash the residue with two or three drops of dilute NH_4OH and two or three drops of water. Centrifuge and add the washings to the liquid which may contain copper and cadmium in the form of $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ ions.

Remove a small portion of the $Bi(OH)_3$ precipitate by introducing a small strip of filter paper attached to a platinum wire. Dip the paper into a solution of sodium stannite (Na_2SnO_2) made by adding NaOH to $SnCl_2$ on a spot plate until the precipitate which first forms disappears. A blackening of the paper indicates bismuth.

A confirmatory test for bismuth may be made by first dissolving the remainder of the $Bi(OH)_3$ in a few drops of dilute HCl and then adding two or three drops of the cinchonine-potassium iodide reagent, the formation of a red precipitate being proof that bismuth is present.

Detection of Copper.—The formation, during the separation of bismuth, of a deep blue solution, which contains the complex copper-ammonia ion, shows the presence of copper. However, if no blue color is observed, the solution should be tested for copper by more sensitive methods. Proceed as follows:

Remove a drop of this solution to a spot plate, acidify with dilute HCl and add a drop of $K_4Fe(CN)_6$ solution. A red precipitate of $Cu_2Fe(CN)_6$ proves the presence of copper.

Place another drop of the solution on drop-reaction paper, add a drop of alcoholic α-benzoin-oxime and hold the spot near the mouth of the concentrated NH_4OH reagent bottle, in order to develop the color. In the presence of copper a green coloration will be obtained.

Separation and Detection of Cadmium.—In the absence of copper, a simple identifying test for cadmium may be carried out by neutralizing, with dilute H_2SO_4, a portion of the solution obtained from the bismuth separation and then passing in H_2S, which will produce a yellow precipitate of CdS if cadmium is present.

In the presence of copper, a separation of cadmium from copper must be resorted to, and for this the cyanide separation is recommended. Add to the solution five drops of KCN solution and then pass in H_2S. A yellow precipitate of CdS shows the presence of cadmium.

Analysis of Division B, Group II

Carefully add **dilute** HCl to the Na_2S_2 solution obtained in the process of subdivision of Group II until it is just acidic. Centrifuge. Remove and discard the supernatant liquid. Add two or three drops of **concentrated** HCl to the residue, boil and add two or three drops of water. Centrifuge and remove the liquid to a test tube; this liquid may contain Sb^{+++} and Sn^{++++}. The residue may consist of HgS, As_2S_5 and S.

Separation and Detection of Mercury.—Wash the residue with water until only a faint acidic reaction is shown by the washings, the first of which should be added to the solution which may contain Sb^{+++} or Sn^{++++}. After washing thoroughly, add three to six drops of dilute NH_4OH to the residue, stir, heat, centrifuge and transfer the supernatant liquid to a centrifuge tube. Wash the residue with several more drops of NH_4OH. Complete extraction of A_2S_5 may be tested for by acidifying a drop of the NH_4OH extract with dilute HCl; a yellow precipitate of As_2S_5 will appear if this compound is present.

If a black residue remains from the NH_4OH treatment, add two drops of concentrated HCl and a crystal of $KClO_3$. Test for mercury as already described in Division A.

Detection of Arsenic.—Add dilute HCl to a portion of the NH_4OH solution until it is acidic, centrifuge, remove and discard the supernatant liquid. A yellow precipitate at this point is a good indication of arsenic. For more definite proof the Gutzeit test is recommended. This test is conducted as follows: Transfer a portion of the arsenate solution to an evolution tube; add a few

granules of zinc and a drop or two of dilute H_2SO_4. Insert a plug of cotton saturated with lead acetate solution near the mouth of the tube. Place over the tube a strip of filter paper which has been moistened with a 1:1 solution of $AgNO_3$. A yellow or gray spot will form, due to the formation of the double salt, $AsAg_3 \cdot AgNO_3$.

Detection of Antimony.—The tests for antimony and tin are made in the antimony-tin solution without further separation. To test for antimony place a drop of the solution on a spot plate and add some crystals of KNO_2 and one or two drops of concentrated HCl. When effervescence has ceased, add a drop of rhodamine B reagent. A change in color from bright red to violet shows the presence of antimony.

Place another drop of the solution on a glass slide and heat it nearly to boiling over the micro flame. Drop into the hot solution a crystal of sodium thiosulfate, $Na_2S_2O_3$. An intense red color forming on the crystals, and consisting of the oxysulfide of antimony, identifies antimony in the sample.

Detection of Tin.—Reduce the tin in a few drops of the solution to the stannous state by adding some magnesium powder. Add a drop of this solution to a drop of a saturated aqueous solution of cacothelin on drop-reaction paper. A violet to red coloration proves the presence of tin.

Place several other drops of the solution being tested for tin on the spot plate and add some granules of zinc. Immerse the bottom of the micro crucible in this liquid and then hold it in the flame. A bluish flame playing on the surface of the unglazed crucible bottom confirms the presence of tin.

Analysis of Group III

This group comprises iron, manganese, chromium, aluminum; nickel, cobalt and zinc. The addition of NH_4OH will precipitate the iron, chromium and aluminum as hydroxides and most of the manganese as $MnO(OH)_2$; this subgroup is designated Division A. Nickel, cobalt and zinc are converted to the complex ammonia ions and referred to as Division B.

Attention has already been called to the interference of anions in the systematic detection of cations. Most of the interfering anions will have been removed in the treatment of the sample

prior to the analysis of Group I, or otherwise taken care of. Oxalates, tartrates and phosphates, however, may be present in the solution from Group II. They interfere mainly for the reason that the barium, strontium and calcium salts of these anions are insoluble in a basic solution, and consequently, when the solution from Group II is made basic with NH_4OH, these salts will precipitate along with the hydroxides of iron, manganese, aluminum and chromium. This means that if any members of Group IV, namely barium, calcium and strontium, are contained in the sample, these alkaline earth cations will be prematurely precipitated and removed, with the ultimate result that they will escape detection in their regular places. Furthermore the presence of tartrates and similar organic substances hinders the complete precipitation of $Cr(OH)_3$ and $Al(OH)_3$. Therefore, if these interfering anions have not yet been tested for, their presence or absence must be established at this point.

The test for oxalates is made as follows: Take a few drops of the solution from Group II, which has previously been boiled to remove H_2S, and add Na_2CO_3 until strongly basic. Centrifuge if a precipitate forms. Make the filtrate slightly acidic with $HC_2H_3O_2$, boil and add an equal volume of saturated $CaSO_4$ solution. If a white precipitate (CaC_2O_4) forms, centrifuge, dissolve the residue in dilute H_2SO_4 and add a *tiny* drop of very dilute $KMnO_4$ solution. The solution will be decolorized if oxalates are present.

Test for tartrates, sugar and similar organic material by heating a small portion of the dry sample with concentrated H_2SO_4. A charring or blackening of the residue and the odor of burnt sugar show the presence of organic material.

Test for phosphates by taking two drops of the filtrate from Group II; boil to remove H_2S, add a drop of concentrated HNO_3, warm, add ammonium molybdate and warm again. A yellow precipitate of ammonium phospho-molybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$, shows the presence of phosphates.

Procedure for the Analysis of Group III in the Absence of Oxalates, Tartrates and Phosphates

Precipitation of Division A.—Place the solution from which Group II has been removed and which may contain members of

this and subsequent groups in a large centrifuge tube. Add about five drops of bromine water to oxidize the iron to the ferric state, and boil to remove the excess of Br_2. Add some solid NH_4Cl to prevent the precipitation of magnesium hydroxide and make distinctly alkaline with concentrated NH_4OH, stir thoroughly with a platinum wire and then centrifuge. The liquid may contain $Ni(NH_3)_4^{++}$, $Co(NH_3)_6^{+++}$, $Zn(NH_3)_4^{++}$ and members of Groups IV and V. Transfer it to a separate centrifuge tube. The residue may contain $Fe(OH)_3$, $MnO(OH)_2$, $Cr(OH)_3$ and $Al(OH)_3$. Wash the residue twice with small portions of equal volumes of concentrated NH_4OH and water; add these washings to the supernatant liquid.

Analysis of Division A, Group III

Separation of Iron and Manganese from Chromium and Aluminum.—Add one to three drops of water to the residue, add the same amount of NaOH solution and then carefully add some powdered Na_2O_2. When effervescence ceases, centrifuge and transfer the supernatant liquid to another centrifuge tube; the residue may contain $Fe(OH)_3$ or $MnO(OH)_2$, the liquid may contain the meta-aluminate, AlO_2^-, ion, and the chromate, $CrO_4^{=}$, ion. Wash the residue with water until only a faint basic reaction is shown.

Dissolve the residue with two to four drops of dilute HNO_3 and one or two drops of 3 per cent H_2O_2. Stir with a platinum wire. Add more H_2O_2 if complete solution is not obtained.

Detection of Iron.—Place a drop of the above solution on a spot plate, add a drop of dilute HCl and one drop of $K_4Fe(CN)_6$. A precipitate of Prussian blue shows the presence of iron.

If this test is doubtful, place another drop on drop-reaction paper and add a drop of KCNS solution. A red color proves the presence of iron. Another sensitive test is with sulfosalicylic acid which gives a violet color in the presence of iron.

Detection of Manganese.—Add a drop of concentrated HNO_3 to another drop of the above solution on a spot plate, and an excess of powdered sodium bismuthate. A purple coloration due to MnO_4^- proves the presence of manganese.

If manganese is present in very small amounts in the original sample, it may escape precipitation with the iron and will accord-

ingly be found with the cobalt and nickel. For this reason, provision is made below for testing for manganese if the above test should be negative.

Detection of Chromium.—Place a drop of the solution which may contain the AlO_2^- and $CrO_4^=$ ions (the solution will be yellow if the chromate ion is present) on a spot plate and add some powdered $Pb(C_2H_3O_2)_2$. A yellow precipitate shows the presence of chromium.

Place another drop of the solution in a test tube; add a drop of concentrated HNO_3 and several drops of hydrogen peroxide. Then run into the mixture an equal volume of ether. A more or less permanent blue color in the ether layer is due to an unstable compound between the chromium and the peroxide and proves the presence of chromium.

Detection of Aluminum.—Add dilute HNO_3 to the remainder of the AlO_2^- and $CrO_4^=$ solution until it is just acid, add solid $NH_4C_2H_3O_2$, five drops of either alizarin, alizarin-S or aluminon reagent, and then NH_4OH until the solution is basic. Centrifuge. A red residue with partial removal of the red color of the solution indicates the presence of aluminum.

Analysis of Division B, Group III

Pass H_2S into the solution containing the nickel, cobalt and zinc and possibly small amounts of manganese until precipitation of sulfides is complete. Centrifuge and remove the supernatant liquid, which may contain Groups IV and V, to a marked centrifuge tube. Wash the residue with warm water, adding the washings to the above liquid.

Dissolve the precipitated sulfides in concentrated HCl to which a small crystal of $KClO_3$ is added.

Detection of Nickel.—Make a drop of the solution on a spot plate ammoniacal with NH_4OH and add dimethylglyoxime. A red precipitate of nickel dimethylglyoxime proves the presence of nickel.

Detection of Cobalt.—On a spot plate make a drop of the solution ammoniacal, then acid with $HC_2H_3O_2$. Add a drop of α-nitroso-β-naphthol solution. A reddish-brown precipitate shows the presence of cobalt.

To another drop on the spot plate add two or three drops of

alcohol and drop in a crystal of NH_4CNS. A blue color proves the presence of cobalt.

Supplementary Test for Manganese.—In the absence of a positive test for manganese in Division A, repeat the test described on page 229 for this cation with drop quantities of this solution.

Detection of Zinc.—To the remainder of the solution add one-half its volume of a 30 per cent solution of NaOH and boil for several minutes. This will precipitate the cobalt, nickel (and manganese) as hydroxides, leaving the zinc in solution as the zincate, $ZnO_2^{=}$, ion. Centrifuge to remove the precipitated hydroxides and test for zinc in the filtrate.

Place a drop of the Orange IV reagent in a test tube, acidify it with a drop of dilute H_2SO_4 and add a few drops of a freshly prepared 2 per cent solution of potassium ferricyanide, $K_3Fe(CN)_6$. A red color should form in the mixture. Then add a drop of the zinc solution. If the mixture now turns green, the presence of zinc is shown.

If cobalti-cyanide test paper is available, add a drop of the solution to a small square of the test paper, roll it in a platinum wire and incinerate it in the flame. A green color proves the presence of zinc.

Analysis of Group III in the Presence of Interfering Anions

(*A*) If oxalates or tartrates were found, whether or not phosphates are also present, use the following procedure:

Evaporate the filtrate from Group II to dryness, add a few drops of concentrated H_2SO_4 and heat until the mass chars. Then add a few drops of concentrated HNO_3 and heat until SO_3 fumes are evolved. Repeat the nitric acid treatment until the solution is practically clear. This treatment will destroy the oxalate and tartrate ions, but at the same time will result in the formation of insoluble $BaSO_4$, $SrSO_4$, $CaSO_4$ and possibly $Cr_2(SO_4)_3$. Cool the solution, dilute with water, transfer to a centrifuge tube and centrifuge. The residue may consist of the sulfates of calcium, barium, strontium and possibly chromium, and the solution may contain the ions of Groups III and V.

The solution should now be analyzed by the regular procedures for Group III and Group V.

The residue, containing the sulfates of barium, strontium,

calcium (Group IV) and possibly chromium must now be fused with five times its bulk of Na_2CO_3, the melt cooled, extracted with boiling water and centrifuged, and the residue, consisting of $BaCO_3$, $SrCO_3$ and $CaCO_3$, analyzed by the procedure for Group IV. Chromium, if not found in the solution with other members of Group III, should be tested for in the filtrate obtained in the removal of the above carbonates.

(*B*) If phosphates have been found, unaccompanied by oxalates or tartrates, the procedure below is followed:

The phosphates of calcium, barium and strontium which are insoluble in basic or neutral solutions are precipitated along with aluminum, ferric iron and chromium when the solution is made ammoniacal, and are not found in their regular places. The phosphates of ferric iron, aluminum and chromium are insoluble in weak acetic acid; those of calcium, barium and strontium are soluble in this weakly acidic solution. If the phosphate is precipitated with Al^{+++}, Cr^{+++} or Fe^{+++} ions, the alkaline earth cations will remain in the filtrate and can be detected in their regular places. In order to insure complete precipitation of the phosphates, ferric ions in the form of $FeCl_3$ are added in excess, as the quantity of the phosphates present in the sample may be in excess of the Al^{+++}, Fe^{+++} and Cr^{+++} ions present. The excess Fe^{+++} ions over that necessary to precipitate the $PO_4^{\equiv}$ ions are removed by the formation of basic ferric acetate, $Fe(OH)_2C_2H_3O_2$.

After phosphates are shown to be present, the next step is to test for iron. Place a drop of the filtrate from Group II on a spot plate with a drop or two of H_2O_2 to oxidize the iron to the ferric state and then add a drop of KCNS. A deep red color shows the presence of iron. This test for iron is necessary at this point because $FeCl_3$ is added later to precipitate the phosphate completely.

Boil the filtrate from Group II to remove H_2S, make just ammoniacal with NH_4OH and then add enough dilute HCl to make the solution slightly acid. Add solid $NH_4C_2H_3O_2$ and two drops of 50 per cent $HC_2H_3O_2$. If sufficient iron is present to precipitate all the phosphate as $FePO_4$ and still leave the solution red, there will be an excess; otherwise add $FeCl_3$ solution, dropwise, until the solution turns red. The red color is due to $Fe(C_2H_3O_2)_3$. Dilute the solution with about ten drops of water and heat to boiling. The boiling will precipitate the excess iron as $Fe(OH)_2C_2H_3O_2$.

The precipitate may consist of $FePO_4$, $AlPO_4$, $CrPO_4$ and $Fe(OH)_2C_2H_3O_2$, and all the phosphate will have been removed from solution. Test the filtrate for the presence of the phosphate ion in the manner mentioned above. When the phosphates are shown to be completely removed analyze the filtrate for Mn^{++}, Ni^{++}, Co^{++}, Zn^{++}, Ca^{++}, Ba^{++} and Sr^{++} and Group V, according to the regular procedure.

Analysis of Group IV

The group is made up of the alkaline earths—barium, strontium and calcium.

To the solution from which Groups I, II and III have been separated, add some solid NH_4Cl, make basic with concentrated NH_4OH and add $(NH_4)_2CO_3$ solution until precipitation is complete. Centrifuge and reserve the supernatant liquid for the analysis of Group V. The residue may contain $CaCO_3$, $BaCO_3$, $SrCO_3$.

Separation of Calcium from Barium and Strontium.—To the precipitated carbonates add just enough dilute HNO_3 to dissolve them. Transfer the solution to a large crucible and gently apply heat until the liquid is evaporated, being careful that spattering does not occur. Apply heat to the dry residue to insure the presence of the anhydrous nitrates. Crush the dried cooled residue and add about 1 cc. of **absolute** acetone, stirring the powder thoroughly. Centrifuge, pipetting off the supernatant liquid which contains the calcium.

Detection of Calcium.—To a drop of the supernatant liquid add a drop of ammonium oxalate, $(NH_4)_2C_2O_4$, solution and five or six drops of water. A white precipitate at this point is probably CaC_2O_4. Dissolve this in a drop of HCl and confirm the presence of calcium by the flame test.

Separation of Barium from Strontium.—Dissolve the residue of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ remaining from the calcium separation in water; add a drop or two of dilute acetic acid and an equal quantity of ammonium acetate solution. Then heat and add dropwise enough dilute K_2CrO_4 reagent to effect the complete precipitation of the barium as $BaCrO_4$. Centrifuge the mixture, using the supernatant liquid for the test for strontium.

Detection of Barium.—If a yellow precipitate forms upon adding K_2CrO_4, it is probably $BaCrO_4$, though this separation is

not sharp. Centrifuge and save the supernatant liquid for the strontium test. Dissolve the residue in nitric acid and confirm the presence of barium by the flame test, the green color produced by a Bunsen or Meker burner being due to barium.

Detection of Strontium.—Add a drop of $(NH_4)_2SO_4$ reagent to a drop of the supernatant liquid. A white precipitate of $SrSO_4$ shows the presence of strontium. Check this by a flame test.

Analysis of Group V

This group properly consists of magnesium, potassium and sodium. The detection of the ammonium ion is also provided for below.

Detection of Magnesium.—Place a drop of the solution from Group IV on a spot plate and add a drop of alkaline *p*-nitrobenzene-azoresorcinol. A blue precipitate shows the presence of magnesium.

Removal of Ammonium Salts.—To the remainder of the solution from Group IV, add dilute HNO_3 until distinctly acidic and then evaporate to dryness in a crucible. Continue heating the dried residue until fumes are no longer given off. After the crucible has cooled, add one or two drops of water, and stir with a platinum wire. Warm the residue if it does not dissolve readily. Use this solution, now free from ammonium salts, for the detection of potassium and sodium.

Detection of Potassium.—Place a drop of the solution on a glass slide and add a little freshly prepared solution of $Na_3Co(NO_2)_6$. A yellow precipitate proves the presence of potassium.

Dip a platinum wire into the remaining solution. Try a flame test, viewing the flame coloration through a blue glass. A violet flame indicates the presence of potassium.

Detection of Sodium.—Add eight drops of zinc uranyl acetate solution to one drop of the solution in a centrifuge tube. A pale yellow precipitate, which may come out slowly, shows the presence of sodium.

Detection of the Ammonium Ion.—Place a small amount of the original sample in a test tube, add an excess of NaOH and then insert a funnel and stopper. Place a strip of moist, neutral litmus paper in the opening of the funnel. Heat the tube gently, being careful that none of the liquid comes in contact with the litmus.

A blue coloration on the paper is a test for ammonia and shows the presence of ammonium salts in the original sample.

C. PROCEDURE FOR THE DETECTION OF ANIONS

No scheme for the microchemical separation of the anions has been developed comparable to that of the cations; in fact, even for ordinary, macro analysis, there is no entirely satisfactory scheme of separation. In most cases, the anions must be tested for individually, in the presence of other anions. A definite order of applying tests, however, has been worked out, such that interferences are minimized.

Certain of the anions are tested for in portions of the original sample, while others must be detected in a specially prepared solution made by boiling the sample with Na_2CO_3. This special solution will hereafter be referred to as the " Prepared Solution." The sodium carbonate treatment converts many of the insoluble salts in the sample into insoluble carbonates and hydroxides, while the anions are transposed into the form of soluble sodium salts. The making of the " Prepared Solution " is here described.

Preparation of the Na_2CO_3 Solution

Make a solution by dissolving about 1 gram of Na_2CO_3 in 5 cc. of water, boiling if necessary to dissolve the salt. Place about 0.1 of a gram of the solid sample (or 1 cc. of the unknown solution) in a small beaker or Erlenmeyer, add the Na_2CO_3 solution and boil for 15 minutes. Decant from the residue as much of the clear solution as possible. **Reserve the residue** for tests for phosphates, fluorides, silicates, sulfides and halides, in case these are not detected by tests made with the prepared solution. The prepared solution, now practically free from interfering cations, is used, wherever specified, for the anion tests.

Detection of the Anions of Group I

Nitrites, cyanides, sulfides, thiosulfates, sulfites and carbonates are included in this group.

Preliminary Examination for Anions Which Yield Volatile Products.—Place a very small amount of the sample in a test tube and add several drops of dilute HCl. Note whether the mixture

effervesces and gases are given off. **Very cautiously** smell the gas and observe its color. Heat the mixture almost to boiling and again observe the result. The indications which one might obtain here are:

1. A colorless, odorless gas, CO_2, due to carbonates.
2. A colorless gas, with odor of burning sulfur, will be SO_2, being produced by the decomposition of either sulfites or thiosulfates.
3. A colorless gas, having the characteristic odor of H_2S, being produced from those sulfides which are acted upon by dilute HCl.
4. The odor of bitter almonds, due to HCN from cyanides.
5. Brown fumes of NO_2, arising from nitrites.
6. The deposition of yellow sulfur due to thiosulfates or to the interaction of SO_2 with H_2S.

Detection of Cyanides.—The odor of HCN, if definitely detected, will reveal the presence of cyanides. A more definite test is conducted in the following manner. Dip a strip of drop-reaction paper into a saturated solution of picric acid and then into a solution of Na_2CO_3. Then add a drop of the prepared solution and dry the paper. A red color shows the presence of cyanides.

Detection of Nitrites.—The appearance of brown fumes obtained during the preliminary test for members of this group is a good indication of the presence of nitrites. This observation should be confirmed by the following test. Place a small amount of the sample in a test tube or in the evolution tube, and add dilute HCl. Hold in the escaping vapors a strip of moistened potassium iodide-starch test paper. The NO_2 reacting with the iodide liberates free iodine, which, with the starch, will color the paper blue if nitrites are present in the sample.

Another test may be conducted as follows: To a drop of the prepared solution, acidified with $HC_2H_3O_2$, add a drop of sulfanilic acid and then a drop of α-naphthylamine solution. A red color shows the presence of nitrites.

Detection of Sulfides.—In a test tube or the evolution tube place a small portion of the sample and add a few drops of dilute HCl. Moisten a strip of lead acetate paper with dilute NaOH and expose it over the mouth of the tube. A blackening of the

paper shows the presence of H_2S. Certain sulfides are not decomposed by dilute HCl and will not respond. If sulfides are suspected and not detected by the test just described, add a few granules of zinc and a few drops of H_2SO_4 to the sample and repeat the lead acetate test.

Detection of Thiosulfates.—The odor of SO_2 accompanied by the precipitation of sulfur when the sample is treated with HCl furnishes clues to the presence of thiosulfates. The sulfur dioxide may, however, have been produced from sulfites and the sulfur formation may not be due solely to thiosulfates. The following test is recommended as being more specific. Place a few particles of antimony trichloride on a glass slide. With dilute HCl carefully neutralize a few drops of the prepared solution, heat and then add a drop of this solution to the antimony trichloride. An intense red or vermilion coloration on the surface of the crystals shows the presence of thiosulfates. The color should not be confused with the orange color of antimony sulfide.

Detection of Sulfites.—Treat a small portion of the original sample with a few drops of dilute HCl in a test tube or evolution tube and hold a drop of dilute $KMnO_4$ solution in the escaping gas. If HCN, NO_2 and H_2S are known to be absent by previous negative tests for cyanides, nitrites and sulfides, and the drop of permanganate is bleached, the presence of SO_2 is shown. This may have been evolved from either sulfites or thiosulfates. If thiosulfates have been shown to be absent, the test definitely shows the presence of a sulfite. In the presence of these interfering anions, the bleaching test is inconclusive, except that it shows the presence of one or more reducing gases.

In the absence of a sulfide, the nitroprusside test may be used. Add on the spot plate, in the following order, a few drops of $ZnSO_4$ solution, a drop of $K_4Fe(CN)_6$, one or two drops of sodium nitroprusside and finally a drop or two of the prepared solution. A red color shows the presence of sulfites, even in the presence of a thiosulfate.

In the presence of a sulfide, prepare a zinc nitroprusside paste in a crucible by adding solid $ZnSO_4$ to one or two drops of sodium nitroprusside solution, and heating the mixture. Moisten a small strip of filter paper with the paste and place it in the funnel of the gas-evolution apparatus. Place a drop of the solution in the test tube and add a drop of saturated $HgCl_2$ solution, made

by saturating a drop of water on a spot plate with $HgCl_2$. After the solution has been allowed to stand for about one minute, add a drop of dilute HCl. Insert the stopper and funnel in the tube, heat and allow the vapors to come in contact with the paste on the filter paper. By means of forceps remove the paper from the funnel and hold it over the mouth of the concentrated NH_4OH bottle in order that the color may be developed by NH_3 fumes. A more or less intensive red coloration of the paste proves the presence of sulfites.

Detection of Carbonates.—If cyanides, sulfides, thiosulfates and sulfites have been shown to be absent from the sample, treat a small portion of the original sample with a few drops of dilute HCl and hold in the escaping gas a drop of $Ba(OH)_2$ solution contained in the loop of a platinum wire. The drop will be rendered turbid by the formation of $BaCO_3$, if the gas is CO_2.

If cyanides have been found in the sample, add a few drops of saturated $HgCl_2$ solution to a portion of the original sample, and then conduct the above test for CO_2.

If sulfides, sulfites or thiosulfates are present, add five drops of 3 per cent H_2O_2, then acidify and test the escaping gas with $Ba(OH)_2$.

Detection of the Anions of Group II

This group includes arsenites, arsenates, phosphates, silicates, fluorides, chromates, sulfates, borates, oxalates and tartrates.

Preliminary Test for the Members of This Group.—Acidify a few drops of the prepared solution with dilute HCl and boil to remove carbon dioxide and the volatile products from Group I. Carefully neutralize the solution with dilute NH_4OH, testing the solution with litmus paper. Then add a drop or two of the $BaCl_2$–$CaCl_2$ group reagent. A yellow precipitate forming here is $BaCrO_4$ and shows the presence of chromates. White precipitates will be due to the barium or calcium salts of the other anions of this group, which may be present in the prepared solution. If the group test is positive, the ions of this group must be tested for individually. Certain phosphates, fluorides and silicates are not well transposed by the sodium carbonate treatment used in making the prepared solution, and if these anions are not detected in portions of the prepared solution by the tests described below, these ions should be tested for in portions of the original sample.

Detection of Arsenites.—Place a few drops of the prepared solution in a centrifuge tube, acidify with a drop of dilute HCl and pass in H_2S. If there is an immediate formation of a yellow precipitate (As_2S_3), the presence of arsenites is shown.

Preliminary Test for Arsenates and Phosphates.—Perform the following test for both arsenates and phosphates. Dip a small strip of filter paper into a drop of the prepared solution. Make a saturated solution of borax on a spot plate. Touch the filter paper to this solution, treat the paper with a 20 per cent $SnCl_2$ solution and then add a drop of $(NH_4)_2MoO_4$ solution. Dry by passing over a flame. In the presence of either arsenates or phosphates a blue coloration will result.

Detection of Arsenates and Phosphates.—If arsenites have been shown by the test with H_2S, centrifuge, discard the precipitate and repeat the H_2S treatment with the solution. This operation may have to be repeated several times until it is certain that all the arsenite has been precipitated and removed. If arsenates are present, there will now be a slow formation of a yellow precipitate, consisting of As_2S_5, As_2S_3 and S, upon further passage of the H_2S. If arsenates are thus indicated, add a crystal or two of KI in order to reduce the arsenate and hasten its precipitation. Centrifuge and set aside the tube and its contents for the phosphate test.

If arsenates are found, test for phosphates in the centrifuged solution from which the arsenate has been removed by H_2S by the following methods:

1. To a few drops of the supernatant liquid, acidified with dilute HNO_3, add two drops of ammonium molybdate reagent. A yellow precipitate, $(NH_4)_3PO_4 \cdot 12MoO_3$, shows the presence of phosphates.

2. In a test tube or on a glass slide make a few drops of the supernatant liquid basic with NH_4OH, and add a drop of magnesia mixture. A white precipitate, $MgNH_4PO_4$, which may form after some time, shows the presence of phosphates.

In the absence of arsenates, tests 1 and 2 for phosphates should be made directly with the prepared solution.

Certain phosphates are not transposed, or only incompletely so, by boiling with Na_2CO_3; hence, if the tests for phosphates are negative, the solid residue left from the Na_2CO_3 treatment should nevertheless be examined for this anion. Take a small portion

of the residue, dissolve it in concentrated HNO_3, boil until brown fumes are no longer given off, evaporate to a small volume and carry out the molybdate test as described above.

The following tests should be made with the prepared solution for arsenates in the absence of phosphates:

1. Neutralize a few drops of the prepared solution with dilute HNO_3 and add a few drops of ammonium molybdate reagent. A yellow precipitate of ammonium arseno-molybdate shows the presence of arsenates.

2. To another small portion of the prepared solution add a few drops of magnesia mixture. A slowly forming white precipitate, $MgNH_4AsO_4$, shows the presence of arsenates.

Detection of Silicates.—Place a drop of the prepared solution in a centrifuge tube, add a drop of dilute NH_4OH and then three to five drops of NH_4NO_3 solution. A gelatinous precipitate, H_2SiO_3, shows the presence of silicates. Repeat the test using one or two drops of concentrated HCl in place of the NH_4OH.

If these tests with the prepared solution are negative, take a small portion of the original sample, fuse it with Na_2CO_3 in a crucible, dissolve the fused mass in dilute HCl and carry out the above test.

To a portion of the original sample, in a lead crucible, add a drop or two of hydrofluoric acid. Hold a bead of water contained in the loop of a platinum wire over the mouth of the crucible. The drop of water will become turbid if silicates are present.

Detection of Fluorides.—Place a small amount of the original sample, several grains of powdered sand (SiO_2) and a drop of concentrated H_2SO_4 in a lead crucible. Hold over the mouth a drop of water contained in the loop of a platinum wire. Gently warm the crucible. If fluorides are present, SiF_4 will be evolved and will cause a turbidity to form in the water drop.

If silicates are absent, coat the lower surface of a small watch glass with molten paraffin or beeswax. Scratch some characters through the wax coating. Then place a small portion of the original sample in a lead crucible, add a drop of concentrated H_2SO_4 and place the watch glass on top of the crucible. Put some cold water in the watch glass. Warm the crucible. After thirty minutes, remove the watch glass, melt off the wax and examine the surface for the etched characters.

In the absence of oxalates, phosphates and sulfates, the zirconium nitrate-alizarin test may be used. Follow the directions given on page 197, using a neutral or acidified portion of the prepared solution.

Detection of Sulfates.—Place a drop of the prepared solution in a centrifuge tube and add a drop of $BaCl_2$ solution. If a precipitate forms, centrifuge, remove the supernatant liquid, wash the precipitate with water and add an excess of concentrated HCl. A white precipitate, $BaSO_4$, insoluble in the acid, is the test for sulfates.

Detection of Borates.—Evaporate about $\frac{1}{2}$ cc. of the prepared solution to dryness in a crucible, add a drop or two of concentrated sulfuric acid and add several drops of methyl alcohol. Ignite the vapors. A green flame shows the presence of borates.

The turmeric test can be made only in the absence of oxidizing agents such as nitrites, chromates and ferricyanides, as well as with a solution that is not too highly colored. If conditions permit perform the following test:

Acidify a drop of the solution to be analyzed with dilute HCl, dip a piece of turmeric paper in the solution and dry the paper by carefully passing it over a flame. Add a 1 per cent solution of NaOH to the paper; a reddish color changing to blue or green on the addition of NaOH proves the presence of borates.

Detection of Oxalates.—Add some solid $Ca(C_2H_3O_2)_2$ to a drop of the prepared solution, made acidic with dilute $HC_2H_3O_2$, in a centrifuge tube. A white precipitate indicates oxalates. Centrifuge, wash the precipitate with warm water, dissolve the residue in one or two drops of H_2SO_4 and add a tiny drop of very dilute $KMnO_4$ solution. Bleaching of the $KMnO_4$ confirms the presence of oxalates.

Detection of Tartrates.—Place a few drops of the prepared solution in a crucible. Evaporate to dryness. Add a drop of concentrated H_2SO_4. A char accompanied by a burnt odor proves the presence of tartrates.

Place a drop of the solution in a clean test tube. Add one drop of $AgNO_3$ solution and one of NaOH. Then add dilute NH_4OH until the precipitate dissolves. Warm gently. The formation of a silver mirror proves the presence of tartrates.

Detection of Chromates.—A colorless prepared solution need not be tested for chromates. If the cation analysis has preceded

the anion analysis, and chromium is absent, chromates need not be tested for. If chromium is not known to be absent, a colored solution should be tested in the following way:

Place a drop of the prepared solution in a test tube, acidify with concentrated HNO_3, add three to five drops of ether and one to three drops of 3 per cent H_2O_2. A blue color in the ether layer proves the presence of chromates.

Detection of the Anions of Group III

The anions of this group properly include ferricyanides, $Fe(CN)_6^{\equiv}$; ferrocyanides, $Fe(CN)_6^{----}$; thiocyanates, CNS^-; iodides, I^-; bromides, Br^-, and chlorides, Cl^-.

To test for the presence or absence of the group as a whole, place several drops of the prepared solution in a centrifuge tube, acidify with dilute HNO_3, heat to boiling and add a drop or two of $AgNO_3$ solution. The formation of a precipitate indicates the presence of at least one member of this group. Centrifuge and examine the residue. $Fe(CN)_6^{\equiv}$ gives reddish-brown $Ag_3Fe(CN)_6$; $Fe(CN)_6^{----}$, CNS^- and Cl^- give white $Ag_4Fe(CN)_6$, AgCNS and AgCl; I^- and Br^- give light yellow AgI and AgBr. If the presence of this group is shown, test for the individual members as indicated below.

Detection of Ferrocyanides.—Acidify with HCl a few drops of the prepared solution in a test tube, and add a drop of $FeCl_3$ solution. A deep blue precipitate or a greenish-blue color indicates the presence of a ferrocyanide. If a precipitate is obtained, centrifuge vigorously, adding NaCl and warming if necessary, until the blue precipitate is practically completely removed from the solution. A red supernatant liquid indicates the presence of thiocyanates, and a brown solution indicates ferricyanides. If the solution is colorless, add several drops of $FeCl_3$ to make sure that an excess of Fe^{+++} is present. The above colors serve as a preliminary test for the CNS^- and $Fe(CN)_6^{\equiv}$ ions; these ions are further identified by the following tests.

Detection of Ferricyanides.—Prepare a dilute solution of $FeSO_4$ on the spot plate and add a drop of this solution to a few drops of the prepared solution which has been acidified with HCl. The formation of a deep blue precipitate indicates the presence of ferricyanides.

Detection of Thiocyanates.—To a few drops of neutral or very slightly acid (HCl) prepared solution in a test tube add an equal volume of a concentrated solution of $Co(NO_3)_2$. Add enough isoamyl alcohol to form a distinguishable layer on top of the solution and shake the mixture. A blue color in the alcohol layer indicates the presence of the CNS^- ion.

Simultaneous Detection of Ferrocyanides, Ferricyanides and Thiocyanates.—Place a drop of saturated $Pb(NO_3)_2$ solution on a square of drop-reaction paper and add a drop of the prepared solution acidified with acetic acid. $Pb_2Fe(CN)_6$ is fixed in the center of the spot, while CNS^- and $Fe(CN)_6^{\equiv}$ move farther out. Add a drop of water to the center of the spot and after it has ceased spreading make, with a capillary pipet, a narrow streak across the spot with a solution of $FeCl_3$. Perpendicular to this streak make a similar one with a freshly prepared solution of $FeSO_4$, and finally place a drop of HCl on the intersection of the two streaks. If all three ions are present, a spot of Prussian blue will appear near the center of the spot along the $FeCl_3$ streak; a little farther out along the same streak will appear the red of $Fe(CNS)_6^{\equiv}$; and at the outer edge of the spot along the $FeSO_4$ streak Turnbull's blue will be seen.

The absence of any one of these three colored areas indicates the absence of ferrocyanides, thiocyanates or ferricyanides, respectively. Oxidizing or reducing agents must not be present when carrying out this procedure.

Detection of Iodides and Bromides.—Slightly acidify with HCl a few drops of the prepared solution in a test tube. Add sufficient chloroform to form a distinguishable layer beneath the solution, and add drop by drop a solution of sodium hypochlorite, shaking the mixture and examining the chloroform layer after the addition of each drop. A violet color indicates the presence of an iodide. If no violet color appears by the time five drops of NaOCl have been added, iodide is absent.

If iodides are thus found, continue the addition of NaOCl and shaking until the violet color has completely disappeared. Then in the presence or absence of iodides add two drops of dilute H_2SO_4 and shake. The appearance of a brown or yellowish-brown color in the chloroform layer indicates the presence of a bromide. It is advisable to compare this color with that obtained by following the above procedure using distilled water instead of

the unknown solution, as the chlorine liberated from the NaOCl by the H_2SO_4 sometimes imparts a yellowish color to the chloroform which may be mistaken for the noticeably different bromine color.

Detection of Chlorides.—In the absence of $Fe(CN)_6^{\equiv}$, CN^-, CNS^- and Br^- acidify a small amount of the prepared solution with HNO_3 and add $AgNO_3$ solution until precipitation is complete. The precipitate may be AgCl, AgI or $Ag_4Fe(CN)_6$. Centrifuge; remove and discard the supernatant liquid and wash the precipitate with dilute HNO_3. Then add a few drops of concentrated NH_4OH, shake, centrifuge quickly since AgI dissolves to some extent on standing, and remove the supernatant liquid to a black spot plate or to a glass slide. Acidify with dilute HNO_3. A white precipitate of AgCl shows the presence of a chloride.

In the presence of any or all other ions, add to the prepared solution, *neutralized* with HNO_3, a few drops of $KMnO_4$ solution, to oxidize $Fe(CN)_6^{----}$ and any other reducing agents, until a faint purple color remains. Centrifuge and discard any precipitate that forms. To the solution add $Hg(NO_3)_2$ solution until precipitation is complete; centrifuge and again discard the precipitate. Make the solution from the above treatment acidic with HNO_3, add $AgNO_3$, centrifuge and discard the liquid. To the precipitate of AgCl add a few drops of concentrated NH_4OH to dissolve the AgCl, then finally remove one or two drops of the liquid to a black spot plate or a glass slide and acidify with dilute HNO_3. The reprecipitation of white AgCl shows the presence of chlorides.

Detection of Acetates.—The tests for acetates are carried out on the water-soluble portion of the sample. Place a few drops of the solution to be tested in a crucible; add several drops of ethyl or isoamyl alcohol, then enough concentrated H_2SO_4 to double the volume and heat carefully. In another crucible perform the same test using a small amount of an acetate solution instead of the unknown. Cautiously smell the contents of the two crucibles and compare the odors. The fruity odor of ethyl or isoamyl acetate indicates the presence of an acetate in the unknown.

To another portion, which has been treated with $Ba(NO_3)_2$ and filtered to remove interfering anions, add, in a crucible, a drop of $La(NO_3)_3$ solution (5 per cent). Then add a drop of a $N/50$ solution of iodine in alcohol and, finally, several drops of

dilute NH_4OH. Slowly heat the crucible to boiling. A blue color, which sometimes appears even before heating, indicates the presence of an acetate in the unknown.

Detection of Nitrates.—The tests are carried out on the water-soluble portion of the sample. In the absence of NO_2^-, I^-, Br^- and Cl^- (large amounts) the brown ring test may be used. Place a crystal of $FeSO_4 \cdot 7H_2O$ on the spot plate, add a drop of the unknown solution and then carefully add a drop of concentrated H_2SO_4, trying to mix the solutions as little as possible. A brown ring surrounding the drop of H_2SO_4 indicates the presence of a nitrate. Ag_2SO_4 may be used to remove the above-mentioned interfering ions, with the exception of NO_2^-.

In the presence of NO_2^- the fornitrol reaction may be utilized. Place on a glass slide a drop of the solution to be tested and add a drop of dilute acetic acid and then a drop of fornitrol reagent. A white crystalline precipitate indicates the presence of a nitrate.

D. THE ANALYSIS OF THE INSOLUBLE RESIDUE

In preparing a solution for the systematic detection of cations, the treatment of the sample with acids will frequently leave a residue of insoluble constituents which resist the action of HNO_3 and HCl, taken singly or in combination as aqua regia. Such insoluble compounds may have been constituents of the original sample or may have been formed by interaction of the ions of soluble components. This residue must be examined before the sample can be considered to be completely analyzed.

An inspection of the solubility table shows that comparatively few substances resist the action of hot concentrated HNO_3. The list includes $BaSO_4$, $SrSO_4$, ($CaSO_4$), $PbSO_4$; the halides of silver and possibly those of lead and mercurous mercury; the sulfides of mercury; the cyanogen compounds of silver and certain other metals; gelatinous silicic acid from decomposable silicates; oxides of tin and antimony. Free sulfur may result from the action of nitric acid on sulfides, and black specks of carbon may be derived from organic matter.

The action of aqua regia following that of nitric acid will dissolve the oxides of antimony and tin and the sulfides of mercury, and transpose, at least partially, the silver halides and complex cyanogen salts into AgCl.

The residue may then consist of the following substances:

$PbSO_4$, ($PbCl_2$)
AgCl, (AgBr, AgI, AgCN, AgCNS, $Ag_3Fe(CN)_6$, $Ag_4Fe(CN)_6$)
$BaSO_4$, $SrSO_4$, ($CaSO_4$)
H_2SiO_3, (SiO_2, silicates)
Sulfur, carbon.

Proceed with the systematic analysis of this residue as follows:

1. Digest a portion of residue with hot $NH_4C_2H_3O_2$ solution to dissolve any $PbCl_2$ and $PbSO_4$ which may be present. Examine the filtrate for Pb^{++}, Cl^- and $SO_4^{=}$ ions.

2. Treat a portion of the residue with NH_4OH. This will dissolve AgCl and some AgBr, and silver can thus be tested for in the filtrate by acidifying it with HNO_3.

3. Roast a portion of the residue in an open dish if particles of black carbon or yellow sulfur are visible. These will be oxidized and removed as CO_2 and SO_2.

4. Mix the roasted residue with 10 times its weight of an equal mixture of Na_2CO_3 and K_2CO_3 in a porcelain crucible and heat over a blast lamp or Meker burner until the fused mass becomes a clear melt. Place the cool crucible in a beaker, cover with water and boil. Crush the residue with a stirring rod. Filter and wash the residue. Test for sulfates in the filtrate by acidifying with HCl and adding $BaCl_2$; a white precipitate of $BaSO_4$ proves the presence of $SO_4^{=}$. Dissolve a portion of the washed residue with dilute HCl and test for the alkaline earth ions in the resulting solution. Add HNO_3 to another portion of the residue, if dark colored, to dissolve metallic silver and test for silver in the filtrate.

5. Test a portion of the dry residue for silicates.

APPENDIX

TABLE OF INTERNATIONAL ATOMIC WEIGHTS OF THE CHEMICAL ELEMENTS, 1936

Element	Symbol	At. Wt.	Element	Symbol	At. Wt.
Aluminum	**Al**	26.97	Molybdenum	Mo	96.0
Antimony	**Sb**	121.76	Neodymium	Nd	144.27
Argon	A	39.944	Neon	Ne	20.183
Arsenic	**As**	74.91	**Nickel**	**Ni**	58.69
Barium	**Ba**	137.36	**Nitrogen**	**N**	14.008
Beryllium	Be	9.02	Osmium	Os	191.5
Bismuth	**Bi**	209.00	**Oxygen**	**O**	16.0000
Boron	**B**	10.82	Palladium	Pd	106.7
Bromine	**Br**	79.916	**Phosphorus**	**P**	31.02
Cadmium	**Cd**	112.41	Platinum	Pt	195.23
Calcium	**Ca**	40.08	**Potassium**	**K**	39.096
Carbon	**C**	12.00	Praseodymium	Pr	140.92
Cerium	Ce	140.13	Protactinium	Pa	231
Cesium	Cs	132.91	Radium	Ra	226.05
Chlorine	**Cl**	35.457	Radon (Niton)	Rn	222.0
Chromium	**Cr**	52.01	Rhenium	Re	186.31
Cobalt	**Co**	58.94	Rhodium	Rh	102.91
Columbium	Cb	92.91	Rubidium	Rb	85.44
Copper	**Cu**	63.57	Ruthenium	Ru	101.7
Dysprosium	Dy	162.46	Samarium	Sa	150.43
Erbium	Er	167.64	Scandium	Sc	45.10
Europium	Eu	152.0	Selenium	Se	78.96
Fluorine	**F**	19.00	**Silicon**	**Si**	28.06
Gadolinium	Gd	157.3	**Silver**	**Ag**	107.880
Gallium	Ga	69.72	**Sodium**	**Na**	22.997
Germanium	Ge	72.60	**Strontium**	**Sr**	87.63
Gold	Au	197.2	**Sulfur**	**S**	32.06
Hafnium	Hf	178.6	Tantalum	Ta	180.88
Helium	He	4.002	Tellurium	Te	127.61
Holmium	Ho	163.5	Terbium	Tb	159.2
Hydrogen	**H**	1.0078	Thallium	Tl	204.39
Indium	In	114.76	Thorium	Th	232.12
Iodine	**I**	126.92	Thulium	Tm	169.4
Iridium	Ir	193.1	**Tin**	**Sn**	118.70
Iron	**Fe**	55.84	Titanium	Ti	47.9
Krypton	Kr	83.7	Tungsten	W	184.0
Lanthanum	La	138.92	Uranium	U	238.14
Lead	**Pb**	207.22	Vanadium	V	50.95
Lithium	Li	6.940	Xenon	Xe	131.3
Lutecium	Lu	175.0	Ytterbium	Yb	173.04
Magnesium	**Mg**	24.32	Yttrium	Y	88.92
Manganese	**Mn**	54.93	**Zinc**	**Zn**	65.38
Mercury	**Hg**	200.61	Zirconium	Zr	91.22

SOLUBILITY TABLE

	Ag^+ (1)	Pb^{++} (1)	Hg_2^{++} (1)	Hg^{++}	Bi^{+++} (2)	Cu^{++}	Cd^{++}	As^{+++}	Sb^{+++} (2)	Sn^{++}	Sn^{++++}	Ni^{++}	Co^{++}	Fe^{++}
Nitrite, NO_2^-	Hot W	W	W	W	—	W	W	—	—	—	—	W	W	—
Sulfide, $S^=$	HNO_3	HNO_3	aq. reg.	aq. reg.	HNO_3	HNO_3	HNO_3	HNO_3	strong HCl	strong HCl	strong HCl	HNO_3	HNO_3	HCl
Sulfite, $SO_3^=$	HNO_3	HNO_3	HNO_3	HCl	—	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Thiosulfate, $S_2O_3^=$	HNO_3	HNO_3	—	—	—	—	W	—	—	W	W	W	W	W
Carbonate, $CO_3^=$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	—	—	HCl	HCl	HCl
Arsenite, $AsO_3^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Arsenate, $AsO_4^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	—	HCl	HCl	HCl	HCl	HCl
Phosphate, $PO_4^{\equiv}$	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	HCl	HCl	HCl	HCl	HCl	HCl
Chromate, $CrO_4^=$	HNO_3	HNO_3	HNO_3	HCl	HCl	W	HCl	—	—	HCl	—	HCl	HCl	—
Sulfate, $SO_4^=$	Sl. W Ins.	Ins.	Sl. W Ins.	Sl. W	Sl. W	W	W	—	HCl	W	—	W	W	W
Borate, $BO_3^{\equiv}$	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	—	HCl	—	HCl	HCl	HCl
Silicate, $SiO_3^=$ (3)	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	—	—	—	HCl	HCl	HCl
Fluoride, F^-	W	Sl. W HNO_3	W	W	HCl	Sl. W HCl	Sl. W HCl	—	Sl. W HCl	W	W	HCl	HCl	Sl. W HCl
Oxalate, $C_2O_4^=$ (4)	HNO_3	HNO_3	HNO_3	HCl	HCl	HCl	HCl	—	HCl	HCl	W	HCl	HCl	HCl
Tartrate, $C_4H_4O_6^=$ (4)	HNO_3	HNO_3	Sl. W HNO_3	HCl	HCl	W	HCl	—	HCl	HCl	W	HCl	W	HCl
Ferricyanide, $Fe(CN)_6^{\equiv}$	Ins.	Ins.	—	Ins.	—	Ins.	Ins.	—	—	Ins.	—	Ins.	Ins.	Ins.
Ferrocyanide, $Fe(CN)_6^{\equiv=}$	Ins.	Ins.	—	—	—	Ins.	Ins.	—	—	—	Ins.	Ins.	Ins.	Ins.
Thiocyanate, CNS^-	Ins.	HNO_3	HNO_3	W	—	HNO_3	HCl	—	—	—	W	W	W	W
Cyanide, CN^-	Ins.	HNO_3	—	W	—	HCl	HCl	—	—	—	—	HNO_3	HNO_3	Ins.
Iodide, I^-	Ins.	Sl. W HNO_3	HNO_3	HCl	HCl	Sl. W	W	W	Hyd. W HCl	W	Hyd. W HCl	W	W	W
Bromide, Br^-	Ins.	Ins.	Sl. HNO_3 Ins.	W	Hyd. W HCl	W	W	W	Hyd. W HCl	W	W	W	W	W
Chloride, Cl^-	Ins.	Hot W Ins.	HNO_3	W	Hyd. W HCl	W	W	W	Hyd. W HCl	W	W	W	W	W
Acetate, $C_2H_3O_2^-$	Sl. W	W	W	W	W	W	W	—	—	W	W	W	W	W
Nitrate, NO_3^-	W	W	Sl. W HNO_3	W	Sl. W (HNO_3)	W	W	—	—	—	—	W	W	W
Oxide, ($O^=$)	HNO_3	HNO_3	HNO_3	HCl	HNO_3	HCl	HCl	HCl	HCl	HCl	Sl. HCl Ins.	HCl	HCl	HCl
Hydroxide, OH^-	HNO_3	HNO_3	—	—	HCl	HCl	HCl	—	HCl	HCl	Ins.	HCl	HCl	HCl

W = water-soluble (solubility at least 1 gram of the salt in 100 cc. of water);
Sl. W = slightly soluble in water (solubility about 0.1 gram per 100 cc. of water);
Hyd. W = hydrolyzed by water yielding a product not soluble in water;
HCl = soluble in hydrochloric acid;
HNO_3 = soluble in nitric acid;
Aq. reg. = soluble in aqua regia;
Ins. = insoluble in acids taken singly or together;
— = compound either does not exist or the proper solvent has not been determined.

SOLUBILITY TABLE (*Continued*)

	Fe^{+++}	Mn^{++}	Al^{+++}	Cr^{+++}	Zn^{++}	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}	NH_4^+	K^+	Na^+	Free Acid (H^+)
Nitrite, NO_2^-	W	W	—	—	W	W	W	W	W	W	W	W	(gas)
Sulfide, $S^=$	HCl	HCl	Hyd. W HCl	Hyd. W HCl	HCl	W	W	W	W	W	W	W	(gas)
Sulfite, $SO_3^=$	—	HCl	HCl	—	HCl	HCl	HCl	HCl	W	W	W	W	(gas)
Thiosulfate, $S_2O_3^=$	—	W	W	—	W	HCl	W	W	W	W	W	W	—
Carbonate, $CO_3^=$	—	HCl	—	—	HCl	HCl	HCl	HCl	Sl. W HCl	W	W	W	(gas)
Arsenite, $AsO_3^{\equiv}$	HCl	HCl	—	—	HCl	HCl	HCl	HCl	HCl	W	W	W	—
Arsenate, $AsO_4^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Phosphate, $PO_4^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(liquid)
Chromate, $CrO_4^=$	W	Sl. W HCl	—	HCl	W	HCl Sl. in HNO_3	W	W	W	W	W	W	(solid)
Sulfate, $SO_4^=$	W	W	W	W	W	Ins.	Ins.	Sl. W Ins.	W	W	W	W	(liquid)
Borate, $BO_3^{\equiv}$	HCl	HCl	HCl	HCl	HCl	HCl	Sl. W HCl	Sl. W HCl	HCl	W	W	W	(solid)
Silicate, $SiO_3^=$ (3)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	(solid)
Fluoride, F^-	Sl. W HCl	HCl	W	W	HCl	Sl. W HCl	HCl	Ins.	HCl	W	W	W	(gas)
Oxalate, $C_2O_4^=$ (4)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	HCl	W	W	W	W	(solid)
Tartrate, $C_4H_4O_6^=$ (4)	W	Sl. W HCl	W	W	HCl	HCl	HCl	HCl	W	W	W	W	(solid)
Ferricyanide, $Fe(CN)_6^{\equiv}$	W	Ins.	—	—	HCl	W	W	W	W	W	W	W	(solid)
Ferrocyanide, $Fe(CN)_6^{==}$	Ins.	HCl	—	—	Ins.	W	W	W	W	W	W	W	(solid)
Thiocyanate, CNS^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Cyanide, CN^-	—	HCl	—	HCl	HCl	Sl. W HCl	W	W	W	W	W	W	(gas)
Iodide, I^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Bromide, Br^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Chloride, Cl^-	W	W	W	W	W	W	W	W	W	W	W	W	(gas)
Acetate, $C_2H_3O_2^-$	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Nitrate, NO_3^-	W	W	W	W	W	W	W	W	W	W	W	W	(liquid)
Oxide, ($O^=$)	HCl	HCl	HCl	HCl	HCl	HCl	HCl	Sl. W HCl	HCl	—	W	W	—
Hydroxide, OH^-	HCl	HCl	HCl	HCl	HCl	W	Sl. W HCl	Sl. W HCl	HCl	W	W	W	(liquid)

(1) Addition of HCl will transpose many salts of silver, lead and mercurous mercury into insoluble chlorides.
(2) Many salts of bismuth and antimony show marked hydrolysis with precipitation of water-insoluble products.
(3) The solubility here refers to freshly precipitated and not to native silicates. Decomposition with acids is accompanied by precipitation of gelatinous silicic acid.
(4) Many tartrates and oxalates are soluble in aqueous solutions containing excess tartrate or oxalate ions.

PERIODIC TABLE OF THE ELEMENTS

Group	0	I	II	III	IV	V	VI	VII	VIII
Type Formulas		$R_2O - RH$	$RO - RH_2$	$R_2O_3 - RH_3$	$RO_2 - RH_4$	$R_2O_5 - RH_3$	$RO_3 - H_2R$	$R_2O_7 - HR$	
Series 1		H 1.0078							
2	He 4.002	Li 6.940	Be 9.02	B 10.82	C 12.00	N 14.008	O 16.0000	F 19.00	
3	Ne 20.183	Na 22.997	Mg 24.32	Al 26.97	Si 28.06	P 31.02	S 32.06	Cl 35.457	
4	A 39.944	K 39.096	Ca 40.08	Sc 45.10	Ti 47.90	V 50.95	Cr 52.01	Mn 54.93	Fe 55.84, Co 58.94, Ni 58.69
5		Cu 63.57	Zn 65.38	Ga 69.72	Ge 72.60	As 74.91	Se 78.96	Br 79.916	
6	Kr 83.7	Rb 85.44	Sr 87.63	Y 88.92	Zr 91.22	Cb 92.91	Mo 96.0		Ru 101.7, Rh 102.91, Pd 106.7
7		Ag 107.880	Cd 112.41	In 114.76	Sn 118.70	Sb 121.76	Te 127.61	I 126.92	
8	Xe 131.3	Cs 132.91	Ba 137.36	La 138.92	Ce 140.13	[Positions between			
9				brackets occupied by elements of the rare earth group					
10			not yet definitely assigned.]		Hf 178.6	Ta 181.4	W 184.0		Os 191.5, Ir 193.1, Pt 195.23
11		Au 197.2	Hg 200.61	Tl 204.39	Pb 207.22	Bi 209.00			
12	Rn 222		Ra 225.97		Th 232.12		U 238.14		

TEST SOLUTIONS OF CATIONS

Make stock test solutions by dissolving the weight given in the last column in water (or acids when indicated) and dilute to one liter. The stock solutions are of such strength that each cubic centimeter contains 10 mg. of the metallic ion. For student use dilute the stock solution with 9 times its volume of water.

Cation	Salt	Grams per Liter
Ag^{+}	$AgNO_3$	15.7
Hg_2^{++}	$Hg_2(NO_3)_2 \cdot H_2O$ (*a*)	14.0
Pb^{++}	$Pb(NO_3)_2$	16.0
Hg^{++}	$Hg(NO_3)_2$ (*a*)	16.0
Bi^{+++}	$Bi(NO_3)_3 \cdot 5H_2O$ (*a*)	23.0
Cu^{++}	$Cu(NO_3)_2 \cdot 6H_2O$	46.5
Cd^{++}	$Cd(NO_3)_2 \cdot 4H_2O$	27.5
As^{+++}	As_2O_3 (*b*)	1.3
As^{+++++}	As_2O_5	15.3
Sb^{+++}	$SbCl_3$ (*b*)	19.0
Sn^{++}	$SnCl_2 \cdot 2H_2O$ (*b*)	19.0
Sn^{++++}	$SnCl_4$	21.8
Ni^{++}	$Ni(NO_3)_2 \cdot 6H_2O$	50.0
Co^{++}	$Co(NO_3)_2 \cdot 6H_2O$	50.0
Mn^{++}	$Mn(NO_3)_2 \cdot 6H_2O$	53.0
Fe^{+++}	$Fe(NO_3)_3 \cdot 9H_2O$	71.5
Al^{+++}	$Al(NO_3)_3 \cdot 9H_2O$	70.0
Cr^{+++}	$Cr(NO_3)_3 \cdot 9H_2O$	77.0
Zn^{++}	$Zn(NO_3)_2 \cdot 6H_2O$	45.5
Ba^{++}	$Ba(NO_3)_2$	19.0
Sr^{++}	$Sr(NO_3)_2$	24.0
Ca^{++}	$Ca(NO_3)_2 \cdot 4H_2O$	59.0
Mg^{++}	$Mg(NO_3)_2 \cdot 6H_2O$	16.0
K^{+}	KNO_3	26.0
Na^{+}	$NaNO_3$	37.0
NH_4^{+}	NH_4NO_3	44.5

(*a*) Use dilute HNO_3 to dissolve the salts.
(*b*) Use dilute HCl to dissolve the salts.

SOLID REAGENTS

p-Amino dimethyl aniline	$NH_2C_6H_4N(CH_3)_2$
Ammonium acetate	$NH_4(C_2H_3O_2)$
Ammonium chloride	NH_4Cl
Ammonium iodide	NH_4I
Ammonium nitrate	NH_4NO_3
Ammonium persulfate	$(NH_4)_2S_2O_8$
Ammonium sodium acid phosphate	NH_4NaHPO_4
Ammonium thiocyanate	NH_4CNS
Antimony trichloride	$SbCl_3$
Borax	$Na_2B_4O_7$
Calcium fluoride	CaF_2
Cobalt acetate	$Co(C_2H_3O_2)_2$
Diphenyl-amine	$(C_6H_5)_2{=}N{-}H$
Ferric chloride	$FeCl_3$
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$
Lead acetate	$Pb(C_2H_3O_2)_2$
Magnesium powder	Mg
Potassium chlorate	$KClO_3$
Potassium dichromate	$K_2Cr_2O_7$
Potassium nitrite	KNO_2
Sodium acetate	$Na(C_2H_3O_2)$
Sodium bismuthate	$NaBiO_3$
Sodium carbonate	Na_2CO_3
Sodium peroxide	Na_2O_2
Sodium thiosulfate	$Na_2S_2O_3$
Zinc (arsenic free)	Zn

TEST PAPERS

Cobalti-cyanide
Lead acetate
Litmus (neutral)
Methyl orange
Starch-potassium iodide
Turmeric

LIQUID REAGENTS

Acetic Acid, $HC_2H_3O_2$, dilute. Dilute 35 cc. of glacial acetic acid to 100 cc. with water.

Acetone, $(CH_3)_2CO$. Absolute.

Alcohol, Isoamyl, $C_5H_{11}OH$. (Test reagent for acetates.)

Alcohol, Methyl, CH_3OH. (Test reagent for borates.)

Aluminon, $C_{19}H_9O_2(COONH_4)_3$ (the ammonium salt of aurin-tri-carboxylic acid). Dissolve 0.1 gram of the dye in 100 cc. of water. (Test reagent for aluminum.)

Ammonium Acetate, $NH_4C_2H_3O_2$. Dissolve 23 grams in 100 cc. of water.

Ammonium Carbonate, $(NH_4)_2CO_3$. Dissolve 10 grams in a mixture of 10 cc. of concentrated NH_4OH and 50 cc. of water and then dilute with water to 100 cc.

Ammonium Hydroxide, NH_4OH, concentrated. Sp. gr. 0.9.

Ammonium Hydroxide, NH_4OH, dilute. Dilute 10 cc. of the concentrated reagent with 20 cc. of water.

Ammonium Molybdate, $(NH_4)_2MoO_4$. Dissolve 15 grams of $(NH_4)_2MoO_4$ in 300 cc. of water and pour into 100 cc. of HNO_3 (sp. gr. 1.2). (Test reagent for phosphates.)

Ammonium Oxalate, $(NH_4)_2C_2O_4$. Dissolve 3.5 grams of $(NH_4)_2C_2O_4 \cdot H_2O$ in 100 cc. of water.

Ammonium Sulfate, $(NH_4)_2SO_4$. Dissolve 13 grams in 100 cc. of water.

Aniline, $C_6H_5NH_2$.

Barium Chloride, $BaCl_2$. Dissolve 12 grams of $BaCl_2 \cdot 2H_2O$ in 100 cc. of water.

Barium Chloride-Calcium Chloride Mixture. Dissolve 25 grams of $BaCl_2 \cdot 2H_2O$ and 10 grams of $CaCl_2$ (anhydrous) in 500 cc. of water. (Group II anion reagent.)

Barium Hydroxide, $Ba(OH)_2$. Saturated solution to be kept in special vessel. (Test reagent for carbonates.)

α-Benzoin-Oxime, $C_6H_5CHOH \cdot CNOH \cdot C_6H_5$. Dissolve 5 grams in 100 cc. of 95 per cent alcohol. (Test reagent for copper.)

Bromine Water, Br_2. Saturated solution.

Cacothelin, $C_{20}H_{22}N_2O_5(NO)_2$. Saturated aqueous solution. Synthesis from brucine: Make a mixture of 4 grams of brucine with 10 cc. of HNO_3 (sp. gr. 1.42) and 100 cc. of water and heat to boiling for 15 minutes. Filter after cooling; wash with water and then with alcohol. Dry over H_2SO_4 in a vacuum desiccator. (Test reagent for tin.)

Calcium Chloride, $CaCl_2$. Dissolve 11 grams of $CaCl_2 \cdot 6H_2O$ in 100 cc. of water.

Chloroform, $CHCl_3$.

Chloroplatinic Acid, H_2PtCl_6. To be dispensed by the instructor.

Cinchonine-Potassium Iodide. Dissolve 1 gram of cinchonine in 100 cc. of water, add a few drops of concentrated HNO_3 and warm until solution takes place. After cooling add 2 grams of KI. (Test reagent for bismuth.)

Cobalt Nitrate, $Co(NO_3)_2$. Saturated solution.

Dimethyl-Amino-Benzylidine-Rhodanine. Dissolve 0.03 gram in 100 cc. of acetone. (Test reagent for silver.)

Dimethylglyoxime, $C_4H_8N_2O_2$. Dissolve 1 gram in 100 cc. of 95 per cent alcohol. (Test reagent for nickel.)

Diphenyl-Carbazide, $[C_6H_5NHNH]_2CO$. Make a cold, saturated solution of the reagent in 90 per cent alcohol, saturate with KCNS and add a few crystals of KI. (Test reagent for mercury.)

Ether, Ethyl, $(C_2H_5)_2O$.

Ferric Chloride, $FeCl_3$. Dissolve 10 grams of $FeCl_3 \cdot 6H_2O$ in 100 cc. of water and add 1 cc. of concentrated HNO_3.

Fornitrol. (1 part nitron, 1 formic acid in 100 cc. water.) (Test reagent for nitrites.)

Fuchsin-Bisulfite Solution. Decolorize a 0.1 per cent solution of fuchsin with $NaHSO_3$. (Test reagent for bromides.)

Hydrochloric Acid, HCl, concentrated. Sp. gr. 1.19.

Hydrochloric Acid, HCl, dilute. Dilute 35 cc. of the concentrated reagent to 100 cc. with water.

Hydrogen Peroxide, H_2O_2. The commercial 3 per cent solution.

Lanthanum Nitrate, $La(NO_3)_3$. A 5 per cent solution. (To be dispensed by instructor.) (Test reagent for acetates.)

Magnesia Mixture. Dissolve 10 grams of $MgCl_2 \cdot 6H_2O$ and 10 grams of NH_4Cl in water, add 5 cc. of concentrated NH_4OH and dilute to 100 cc.

Mercuric Chloride. Dissolve 5.0 grams in 100 cc. of water.

Mercuric Nitrate, $Hg(NO_3)_2$. Dissolve 10 grams of the salt in 99 cc. of water and add 1 cc. of concentrated HNO_3.

Nitric Acid, HNO_3, concentrated. Sp. gr. 1.42.

Nitric Acid, HNO_3, dilute. Dilute 35 cc. of the concentrated reagent to 100 cc.

α-Nitrobenzene-Azo-Resorcinol, $C_{12}H_9N_3O_4$. Dissolve 0.001 gram of the substance in 100 cc. of 2 N NaOH. (Test reagent for magnesium.)

α-Nitroso-β-Naphthol, $C_{10}H_6OH(NO)$. Make a saturated solution of the reagent in 50 per cent acetic acid. (Test reagent for cobalt.)

Orange IV. Dissolve 0.01 gram of Tropeolin OO in 100 cc. of water. (Test reagent for zinc.)

Picric Acid, $C_6H_2OH(NO_2)_3$. Saturated solution in water.

Potassium Chromate, K_2CrO_4. Dissolve 10 grams of K_2CrO_4 in 100 cc. of water. (Test reagent for lead and barium.)

Potassium Cyanide, KCN. Dissolve 5 grams in 100 cc. of water.

Potassium Ferricyanide, $K_3Fe(CN)_6$. 10 grams in 100 cc. of water.

Potassium Ferrocyanide, $K_4Fe(CN)_6$. 10 grams in 100 cc. of water.

Potassium Permanganate, $KMnO_4$. Dissolve 1.6 grams in 100 cc. of water.

Rhodamine B. Dissolve 0.01 gram in 100 cc. of water. (Test reagent for antimony.)

Silver Nitrate, $AgNO_3$. 1.7 grams in 100 cc. of water.

Silver Sulfate, Ag_2SO_4. Saturated solution.

Sodium Acetate, $NaC_2H_3O_2$. Saturated solution.

Sodium Cobaltinitrite, $Na_3Co(NO_2)_6$. Dissolve 100 grams of $NaNO_2$ in 300 cc. of water; add 10 cc. of acetic acid and 10 grams of $Co(NO_3)_2 \cdot 6H_2O$. Allow to stand a day and filter if necessary. Fresh reagent must be prepared frequently since it is somewhat unstable.

Sodium Hydrogen Phosphate, Na_2HPO_4. Dissolve 12 grams of $Na_2HPO_4 \cdot 12H_2O$ in 100 cc. of water.

Sodium Hydroxide, NaOH. 25 grams dissolved in 100 cc. of water.

Sodium Hypochlorite, NaOCl. Commercial Zonite will serve the purpose.

Sodium Nitroprusside, $Na_2Fe(CN)_5NO$. Dissolve 1 gram in 100 cc. of water.

Sodium Polysulfide, Na_2S_2. Dissolve 48 grams of $Na_2S \cdot 9H_2O$ and 4 grams of NaOH in water, add 1.6 grams of sulfur, shake until all the sulfur is dissolved and dilute to 100 cc.

Stannous Chloride, $SnCl_2$. Dissolve 20 grams of $SnCl_2$ in 100 cc. of dilute HCl.

Sulfanilic Acid-α-Naphthylamine. Dissolve 0.5 gram of sulfanilic acid, $NH_2C_6H_4SO_3H$, in 150 cc. of 10 per cent acetic acid (Reagent A). Boil 0.1 gram of α-naphthylamine with 20 cc. of distilled water (Reagent B). (Reagents A and B used in test for nitrites.)

Sulfosalicylic Acid. Dissolve 5 grams in 100 cc. of water.

Sulfuric Acid, H_2SO_4, concentrated. Sp. gr. 1.84.

Sulfuric Acid, H_2SO_4, dilute. Pour 20 cc. of the concentrated reagent, slowly and with constant stirring, into 80 cc. of water.

Tetra-Methyl-Diamino-Diphenyl-Methane, $CH_2[C_6H_4N(CH_3)_2]_2$. Dissolve 0.05 gram in 10 cc. of glacial acetic acid and dilute to 100 cc. with water. (Test reagent for lead.)

Thiosin-amine, $NH_2CSNH(CH_2CH{-}CH_2)$. Dissolve 5 grams of the reagent in 100 cc. of water. (Test reagent for cadmium.)

Zinc Sulfate, $ZnSO_4$. Saturated solution.

Zinc-Uranyl-Acetate. Dissolve 10 grams of uranyl acetate in 6 grams of 30 per cent acetic acid, warming, if necessary, and dilute to 50 cc. In a separate vessel mix 30 grams of zinc acetate with 3 grams of 30 per cent acetic acid and dilute to 50 cc. Mix these two solutions, add a pinch of NaCl, allow to stand 24 hours and then filter. (Test reagent for sodium.)

Zirconium Nitrate, $Zr(NO_3)_4$. Dissolve 50 mg. of $Zr(NO_3)_4$ in 50 cc. of H_2O and add 5 cc. of HCl.

APPARATUS LIST

Each student's locker should contain the following equipment. Upon being assigned a locker, carefully check over the contents and report shortages and imperfect apparatus to the instructor.

Non-Returnable List

4 sheets drop-reaction paper.
2 crucibles (1 cc.).
6 medicine droppers.
1 platinum wire.
1 length glass tubing.
1 slide holder.
1 pair tweezers.
1 nichrome wire triangle.
1 towel.
1 sponge.
1 box matches.
1 two-hole rubber stopper to fit 50-cc. Erlenmeyer flask.
1 nickel wire spatula.
1 box labels No. 4007.
1 square of sheet lead (dented to make crucible).

Returnable List

12 test tubes (2 cc.)
4 centrifuge tubes (3 cc.).
4 " " (2 cc.).
4 " " (1 cc.).
2 small watch glasses.
1 reagent block—60 tubes and corks.
12 microscope slides.
1 cobalt glass.
1 white spot plate.
1 black spot plate.
1 micro burner.
1 500-cc. wide-mouth bottle.
1 500-cc. beaker.
1 50-cc. Erlenmeyer flask.
1 micro funnel.
1 ringstand.
1 regular test tube.
1 10-cc. graduate.
1 buret clamp.
1 ring.
1 100-cc. beaker.
12 30-cc. bottles with droppers.
48 screw cap vials with dropping tubes.
36 biological vials with corks.

AUTHOR INDEX

The superscript designates the number of the reference on the page indicated.

SUBJECT INDEX